Stabilization of Raney Nickel Catalyst for Fuel Cell Electrodes

by

Shaik MMJ Kareemuddin

A Thesis Presented to the

FACULTY OF THE COLLEGE OF GRADUATE STUDIES

KING FAHD UNIVERSITY OF PETROLEUM & MINERALS

DHAHRAN, SAUDI ARABIA

In Partial Fulfillment of the
Requirements for the Degree of

MASTER OF SCIENCE

In

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This thesis, written by Mr. Shaik MMJ Kareemuddin under the direction of his Thesis Advisor and approved by his Thesis Committee, has been presented to and accepted by the Dean of the College of Graduate Studies, in partial fulfillment of the requirements for the degree of MASTER OF SCIENCE in Chemical Engineering,

Thesis Committee:

Dr. Muhammed A. Al - Saleh
Thesis Advisor

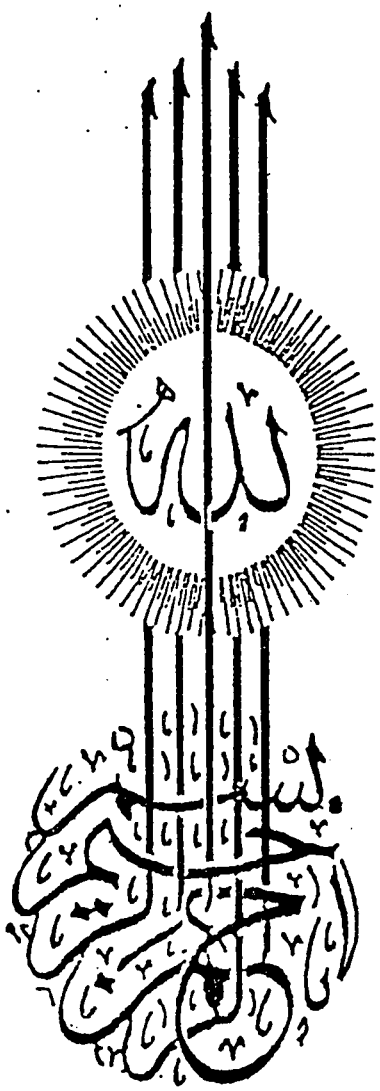
Dr. Abdullah S. Al - Zakri
Member

Prof. Hussain K. Abdel Aal
Member

Dr. Dulaihan K. Al - Harbi
Department Chairman

Dr. Ala H. Al - Rabeh
Dean, College of Graduate Studies

Date: Jan. 24, 1996



سُبْحَانَكَ لَا عِلْمَ لَنَآ إِلَّا مَا عَلَّمْتَنَآ ۖ إِنَّكَ أَنتَ ٱلْعَلِيمُ ٱلْحَكِيمُ

(Glory to Thee: Of knowledge we have none, save what Thou hast taught us: In truth, it is Thou who art perfect in knowledge and wisdom.)

(2:32)

صدق الله العظيم

TO MY FATHER, MOTHER, ZAINAB AND KHADER ALI

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SHAIK MMJ KAREEMUDDIN
Dhahran
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ملخص الاطروحه

تمت دراسة طريقتين لإقرار النيكل الاسفنجي المستعمل في أقطاب خلايا الوقود . الطريقة الإولى هي باستعمال ثاني أكسيد الهيدروجين وأما الثانيه فهي بطريقة الاكسده المباشره . من مزايا هذه الوسائل هي تقليص أحتمال تلبد العامل المساعد وتخفيض التكلفه بالاضافه الى توفير الوقت بالمقارنه بالطرق التقليديه .

عند عملية إستخلاص الالمنيوم باستعمال محلول قاعدي ينتج عنه الهيدروجين والذي بدوره يمتز على سطح النيكل الاسفنجي . وعند تعرض العامل المساعد للهواء يتأكسد هذا الهيدروجين وينتج الحراره مما يسبب تلبيد العامل المساعد ، ولذلك لابد من أقرار العامل المساعد قبل استعماله . الطريقه التقليدية المستعمله حاليا هي القيام بتجفيف العامل المساعد في فرن خاص ومن ثم تعريضه لكميات قليله عن لاكسجين لازالة الهيدورجين وتكوين طبقة سطحية حامية من اكسيد النيكل .

إن ثاني اكسيد الهيدروجين يتحلل بوجود الماء الى اكسجين والذي يقوم باكسده النيكل الاسفنجي حيث ينتج كميات كبيره من الطاقة الحراريه من هذا التفاعل ولكن بوجود التفاعل في وسط مائي أمكن التحكم بالحرارة لتقليل أمكانيه حدوث التلبد .

وأما الطريقة المباشره للاكسده فهي تعتمد على تمرير غاز الاكسجين خلال الماء المحتوي على حبيبات النيكل الاسفنجي العالقه . لقد وجد أيضاً تكوين طبقه سطحيه من أكسيد النيكل بهذه الطريقه .

لقد تم تحليل العينات المختلفه بالطرق السطحيه لمعرفة الخواص الطبيعيه للعامل المساعد بعد تثبيته . لقد وجد أن عملية الاقرار بواسطة ثاني أكسيد الهيدروجين أكثر كفاءة من الطرق الأخرى حيث يحتوي العامل المساعد على مساحه سطحيه أكثر وأكسيد النيكل المستقر وأفضل توزيع للثقوب وأما العامل المساعد المنتج بواسطة الاكسده المباشره فهو أقل نشاطاً من الطريقه التقليديه .

لقد تم أستعمال طريقة الترشيح في تحضير خلايا الأقطاب الغازيه بأستعمال النيكل الأسفنجي المثبت بالطرق المختلفه .حيث قيس أداء هذه الأقطاب في نصف خليه . النتائج المستحصله أشارت إلى أن العامل المساعد المنتج بالتثبيت عند ١٥٪ ثاني أكسيد الهيدروجين ينتج أفضل قطب غازي مقارنه بالطرق الأخرى . كما تمت دراسة الأداء الطويله الأجل لهذه القطب حيث لم يبدى أي تناقص في أداءه خلال المده المدروسه .

درجة الماجستير فى الهندسه الكيميائية

جامعة الملك فهد للبترول والمعادن

الظهران - ٣١٢٦١

المملكة العربية السعودية

THESIS ABSTRACT

NAME : SHAIK MMJ KAREEMUDDIN
TITLE : Stabilization of Raney Nickel catalyst for Fuel Cell electrodes.
MAJOR : CHEMICAL ENGINEERING
DATE : DECEMBER, 1995

Two new methods namely, Hydrogen peroxide oxidation and Direct Gas oxidation have been proposed and studied for the stabilization of Raney Nickel catalyst used in Fuel Cell electrodes which eliminate the possibility of catalyst sintering that is usually encounters in conventional controlled surface oxidation method.

Raney Nickel catalyst needs to be stabilized as it contains adsorbed hydrogen on its active sites which has to be removed to avoid sintering. In conventional method, dried catalyst in vacuum oven is reacted with small doses of oxygen to remove the adsorbed hydrogen and to form a NiO layer on the catalyst.

Hydrogen peroxide oxidation process utilizes the oxygen in the H_2O_2 to react with chemisorbed hydrogen. Direct Gas oxidation process utilizes the pure oxygen or air to remove the adsorbed hydrogen.

Characterization of the stabilized catalysts has also been done using SEM, XRD, BET surface and pore size distribution. The H_2O_2 stabilized catalysts have better active surface area, stable NiO content and good pore size distribution compared to conventional process. Direct Gas oxidation catalysts have shown relatively less activity compares to conventional catalysts because of their unstable NiO content.

Filtration method was used for preparing electrodes. Electrode performance has been found by using Half cell arrangement connected to Potentioscan interfaced with computer. Results showed that 15 wt.% H_2O_2 stabilized catalysts have shown better performance than the other electrodes. The Direct Gas oxidation electrodes have shown poor performance compared to conventional electrodes.

Long term performance and reproducibility tests of 15 wt.% H_2O_2 stabilized electrodes have been carried out and found to be successful.

MASTER OF SCIENCE DEGREE
KING FAHD UNIVERSITY OF PETROLEUM AND MINERALS
Dhahran - 31261, Kingdom of Saudi Arabia.

CHAPTER # 1

INTRODUCTION

1.1. Definition of a Fuel Cell

A Fuel Cell is an electrochemical device composed of a non consumable anode and cathode, an electrolyte, and suitable controls. The free energy of the reactants, which are stored outside the cell, is converted in to electrical energy. Fundamentally any oxidation-reduction reaction may be a potential fuel cell. Perhaps the most highly refined fuel cell system today is the human body, a mechanism that is catalytically (enzymes) burns (oxidizes) food (fuel) in an electrolyte (blood), to produce energy, some of which is electrical (1).

The oxidation of fuel at the anode and simultaneous reduction of oxidant at the cathode causes a potential difference. The potential difference promotes electron flow in an external circuit, where a load is connected. Thus useful work is obtained form fuel cell by physical

separation of the electrode processes. To keep the electrolyte invariant the reaction products are discarded.(2).

Theoretically any spontaneous chemical reaction can be used in a fuel cell. Because of unlimited supply of oxygen in air, combustion reactions are usually preferred. Most of the system under development rely on hydrogen as fuel(2).

1.2. Classification of Fuel Cells

Fuel cells can be classified as high, medium, or low temperature cells. High temperature fuel cells are typified by molten salt electrolyte systems, 1100-1200°F., medium temperature by the Bacon hydrogen - oxygen cell, 400 F, and low temperature by any number of hydrogen - oxygen systems that operate up to the boiling point of the aqueous electrolyte.

Classification by electrolyte designates either basic are acidic systems. A variety of acids and bases have been investigated. Classification by form of electrolyte could include solid electrolyte, or a contained electrolyte. In the later case, capillary membranes such as asbestos, or ion exchange membranes are the most common.

Fuel cells can be classified by the form of the fuel. Gaseous fuel is typified by hydrogen, liquid by alcohol, and solid by coal or metals. And finally, there is classification by the individual fuel; itself. Most Discussion to the date have tended to classify fuel cells by form of

electrolyte and this parameters have served its purpose. However, classification by fuel is most indicative because fuel cell technology is branched out in to many more fuels than heretofore. Also, the cell configuration and technology is controlled primarily by this factor.

It should be noted that oxidants for the use in cells in general are limited to oxygen, air, and hydrogen peroxide. Air and oxygen can usually be used, however, a power loss of 40 - 50 % is realized when air is substituted for oxygen in a low temperature system(1). Hydrogen peroxide with a suitably passivated electrodes is a convenient oxidant, particularly in liquid cells(1). Table 1.1 and 1.2 shows the classification of fuel cells on the basis of electrolyte and on the basis of usage and material of construction respectively.

1.3 Advantages and limitations of Fuel Cells

The advantages of fuel cells as power producers have captured the fancy of the layman as well as the technologists. Following are some of the advantages of these typical low temperature devices.

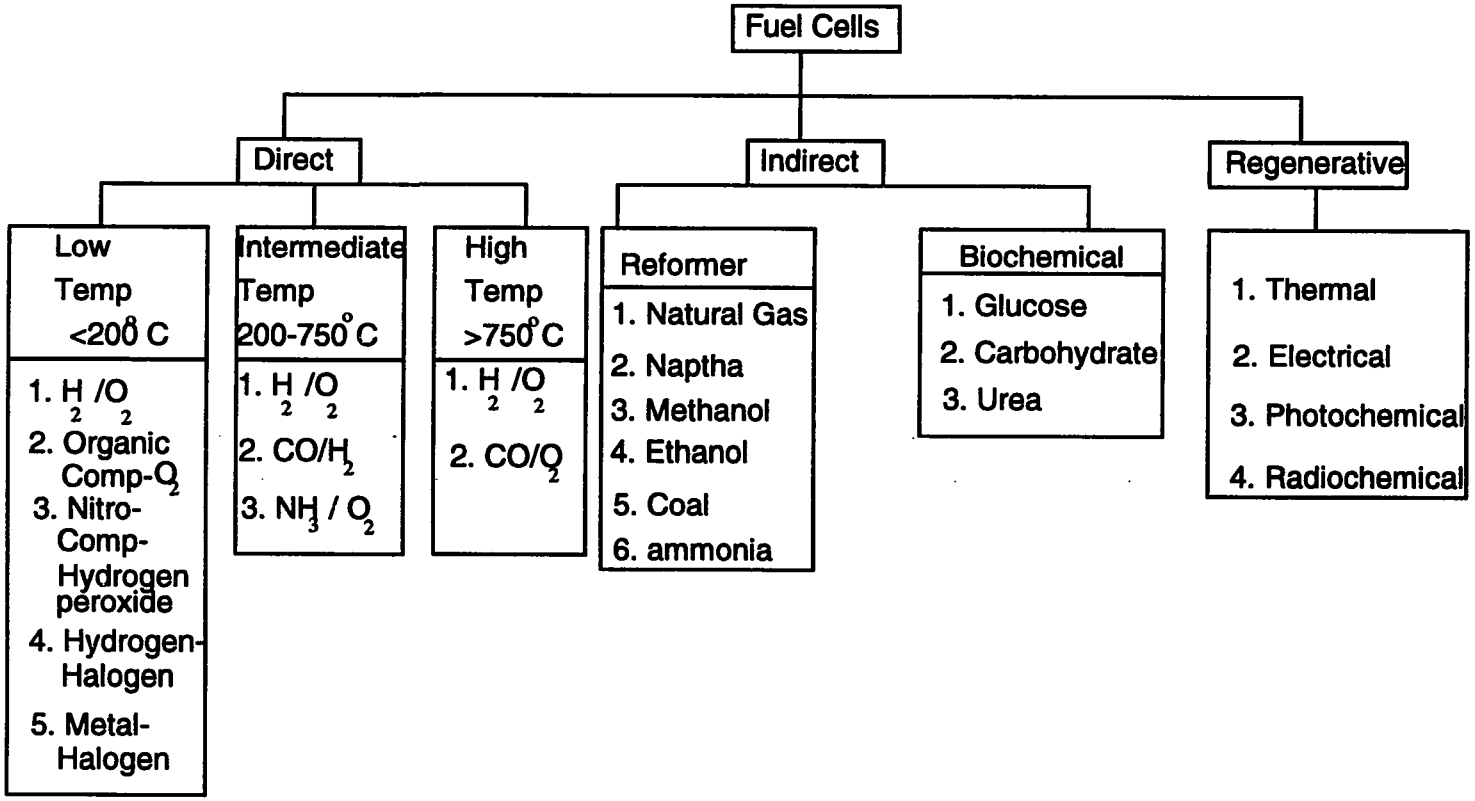
a) Efficiency :

Since chemical energy is directly converting in to electricity without a preliminary conversion in to heat, it is not subjected to Carnot limitations, and thermal efficiencies as high as 90% are theoretically possible. Also in passing chemical energy in to electricity

TABLE 1.1 : Classification of Fuel Cells on the Basis of Electrolyte

	Alkaline Fuel Cell (AFC)	Phosphoric Acid Fuel-Cell (PAFC)	Solid Oxide Fuel Cell (SFC)	Solid Polymer Electrolyte Fuel Cell	Molten Carbonate Fuel Cell
Electrolyte	NaOH or KOH	o-Phosphoric Acid	Ion-conducting oxides(ZrOwithYO)	Ion-Conducting Membrane	KLiC (Molten)
Fuel	Pure H_2	H_2 and CO	H_2 and CO	Pure H_2	H_2 and CO
Operating Temperature	<100 °C	<200 °C	800-1000 °C	<100 °C	~800 °C
Electrode Material	Metal or Carbon	Carbon	Ceramics	Carbon	Metal-based
Configuration	Mono/bipolar	Bipolar	Mono/bipolar	Mono/bipolar	Bipolar

TABLE 1.2 : Classification of Fuel Cell



no mechanical conversion is required such as boiler to turbine and turbine to generator systems, with their inherent losses.

b) Flexibility in power plant design :

The current generated by an individual cell is proportional to the geometrical area of the electrode; hence, to increase the current, the electrode may be increased in size, or several cells may be connected in series or in parallel to attain very high voltages. This flexibility is most important in design point of view.

c) Manufacturing :

The manufacturing cost of fuel cell is low as compared to engines, where close tolerances are required. There are no moving parts in cell, hence sealing problems are minimum and no bearing problem exists. Fuel and oxidant manifolds and diffusers can be punched, or cast in metal or plastic. The whole system of cells and controls, etc., is amenable to mass production methods of manufacture.

d) Maintenance :

Because there are no moving parts, most fuel cells present little or no maintenance problems. Wear and tear, aging, corrosion etc., are no more aggravated in fuel cells than in comparable to battery systems. In high temperature cells corrosion is still a serious problem; in low

temperature cells corrosion is less worrisome. Fuel cells can provide long, trouble-free life. Low noise, no heating problem, cleanliness and reliability are other promising features of fuel cells.

Limitations of Fuel Cells :

The limitation of fuel cells include actual efficiency, reliability and overall cost. Sources of irreversible behavior such as ohmic losses and sluggish kinetics limit the fuel cell efficiency below 50%. The specific power obtained from fuel cell is very low. Other disadvantages of fuel cell include larger weight and volume of gas fuel storage system, liquefaction expenses for the fuel, cleaning requirements for the reactants, deactivation of the electrode catalyst, etc., (3).

1.4. Applications of Fuel Cells

The fuel cell was practically used first time in Gemini spacecraft of 1960s. This followed by a chain of spacecraft with fuel cells including Apollo and Space Shuttle. Their excellent energy output per weight and the fact that the water is the only by-product make them important for space applications. Applications that can best absorb the relatively high capital cost or in which benefits of using the fuel cells compensate the

high initial cost will be most likely, the most practical in future. Table 1.3 lists their potential applications together with their relative importance (4). Remote power applications include submarine,

TABLE 1.3 : Potential Fuel Cell applications

Application		Efficiency		Emission/Noise		Cost
		Weight/Volume	Fuel Cost	Environmental	Detectibality	
Remote	Space	2	3	3	3	3
	Submarine	1-2	2	3	2	2-3
Portable	Military	1-2	3	3	2	2-3
	Recreational	3	2	3	3	1
Utility	Small(<1 MW)	3	2	2	3	1-2
	Large	3	2	2	3	2
Other	Emergency	3	3	2	3	1
	Transportation	1	2	2	3	1

Where : 1= Very Important, difficult to achieve targets.

2= Very important, targets achievable.

3= Relatively unimportant (compared with other requirements)

navigation aids, automatic weather stations, remote beacons, pipeline cathodic protection and communication etc. As portable power generation they compete with diesel engines. Their reliability, system weight, fuel efficiency and nondetectability give them upper hand in military usage. Utility is another important area where fuel cells are being used. These applications can be classified into the following three categories :

a: On-site power plant requiring 40-400 kW
b: Electric Power Plants (5-50 MW)
c: Electric Power Plants (100-500 MW)

Transportation is among the attractive applications of fuel cells. But commercially successful fuel cell base transportation systems demand inexpensive fuel cells. Table 1.4 shows threshold capital cost for different applications. This suggests the easy commercial uses will involve electric utility, on site and cogeneration units (4).

1.5. H_2/O_2 Alkaline Fuel Cells

Among the low temperature H_2/O_2 fuel cells alkaline fuel cells with KOH and acidic fuel cells with phosphoric acid are the most important. Alkaline fuel cells have several advantages over the acidic ones. Among these are better cathode performance, lower cost of material of construction and lesser corrosion. One of their major

TABLE 1.4 : Threshold Capital Values for different Fuel cell Applications

Applications	Threshold Cost (1984 $ per kW installed)
Space	>10,000
Military	4,000
Utility Small (<1MW)	2,000*
Utility Large	1,500*
Emergency Power	1,000
Transportation	100

* Includes industrial cogeneration.

problems is formation of carbonates with carbon dioxide impurity in the fuel or oxidant (5). Although there are not much cost data available, alkaline fuel cells are considered more beneficial for low temperature applications (6). In this study attention is focused on alkaline H_2/O_2 cell with KOH as electrolyte. A typical H_2/O_2 fuel cell operation and conventions are shown in Fig. 1.1. At the anode, hydrogen is oxidized to form water and simultaneously at the cathode, oxygen is reduced to form hydroxyl ions. Electrons are released in the process and they flow in the external circuit. The charge transfer takes place through the electrolyte by hydroxyl ions. The electrode reactions and the overall reaction of this process are as follows :

Anodic Reaction $H_2(g) + 2OH^-(aq) \longleftrightarrow 2H_2O + 2e$

Cathodic Reaction $\frac{1}{2}O_2(g) + H_2O(l) + 2e^- \longleftrightarrow 2OH^-(aq)$

Overall Reaction $H_2(g) + O_{2(g)} \longrightarrow H_2O$

$\Delta G° = -56.7$ kcal

$\Delta H° = -68.3$ kcal

$E° = 1.229$ V

If non-porous planer electrode is used in a fuel-cell using gaseous reactants, the current densities produced are of the order of micro to milli amperes per square centimeter. These values are too small to be used in a practical fuel-cell system. This neccecciates the use of porous electrodes. A good electrode structure must be able to bring gas and

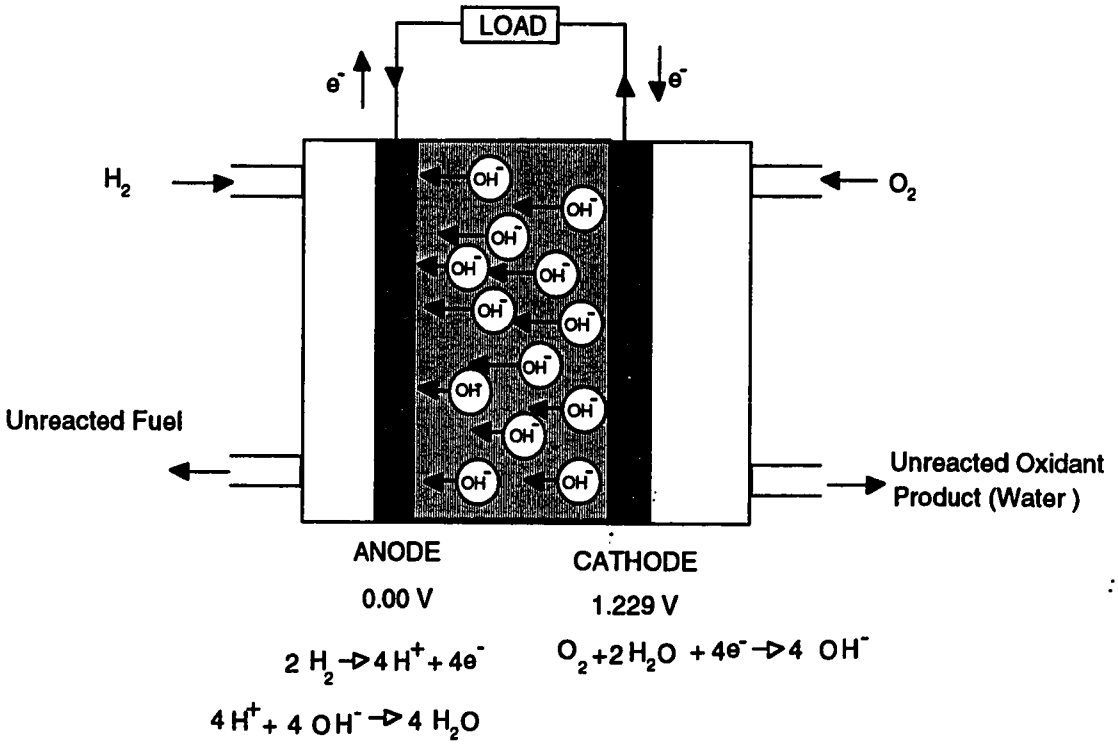


Fig. 1.1 Schematic Diagram Of Alkaline Fuel Cell

electrolyte together so that the reaction can be easy and rapid and must be able to keep them apart to prevent undesirable mass-transfer such as bubbling, floating or weeping. This is another reason why enlarged surface area and porous structure are required for gas diffusion electrodes.

1.6 Electrode kinetics and Modes of Polarization

The passage of electric current through a fuel-cell changes the potential of the electrode. This phenomenon is known as polarization. The difference between the potential at a particular current density and the open circuit potential is the overpotential of an electrode. In a fuel-cell the working potential is lesser than the rest potential. A typical polarization curve is shown in Fig. 1.2 for hydrogen-oxygen fuel-cell. It is evident that the overpotential is a measure of total losses occurring in the different processes in the fuel-cell. Therefore a polarization curve is an index of the performance of the electrodes and the cells. Smaller overpotential at a given current density indicate more efficient electrode. The overall overpotential of a cell is a result of a number of processes occurring in the fuel-cell. There can be losses in different locations.

1.7 Preparation of electrodes:

There are two methods called 'Wet method' and 'Dry method' for making single layered, hydrophobic, PTFE bonded electrodes(24). Wet method utilizes expensive PTFE emulsion whereas Dry method

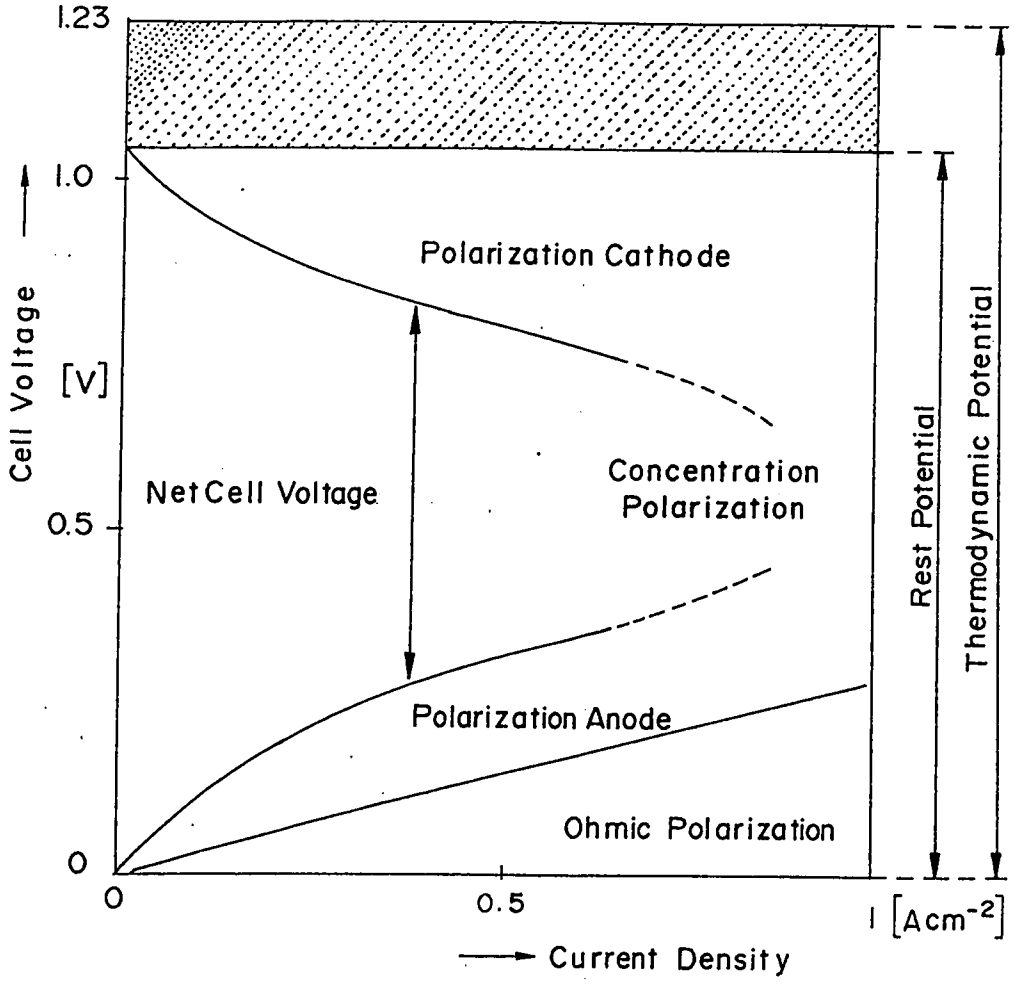


Fig. 1.2 : A Typical Hydrogen - Oxygen Fuel - Cell Polarization curve

electrodes are cheap and thin. But, the activity of electrode made by dry method is less compared to wet method. To overcome these problems, Filtration method(7) is used in making electrodes. Working electrode is prepared by using Raney - Ni catalyst which is obtained by leaching aluminum from NiAl alloy. Hydrogen liberated in the leaching reaction has a tendency of getting adsorbed in the microporous structure of the catalyst. This hydrogen, when the dry catalyst is exposed to air, will react with oxygen. As this reaction exothermic, considerable heat will be liberated and the catalyst will sinter. This characteristic, known as pyrophoricity, of the catalyst can be eliminated by conventional controlled surface oxidation. This method utilizes careful oxidation of the adsorbed hydrogen as well Ni under controlled pressure and temperature conditions. The resulting, stabilized catalyst is mixed with desired amount of PTFE powder. Surfactant is added to make the slurry of the mixture. The slurry is filtered through a filter paper. The filter cake thus formed is rolled on a nickel mesh to make final electrode.

1.8. Methods and techniques for Fuel-cell studies

A complete fuel-cell is used for initial screening for life testing by studying the performance of fuel and oxidant electrodes over extended periods of time. On the other hand, using a half-cell, the reaction on each electrodes can be studied separately. In this case it is necessary to supply current from an external source. The overall reaction taking place in this half cell is not the same as that occurring in

the complete cell. A schematic diagram for the operation of a half cell is shown in Fig. 1.3. The cell is provided with a reference electrode and a counter electrode besides a working electrode assembly which comprises the electrode to be studied. The half cell is placed in a thermostat bath. It is also possible to measure IR-free potential of the electrode using current interruption or positive feedback techniques. In this work , the experiments are carried out using a half cell and the IR-drop is found using current interruption technique.

1.9 Objectives of this study

The main objective of the study is the stabilization of pyrophoric Raney - Ni catalyst, which is a major part in electrode manufacturing. As this pyrophoricity results in sintering of the catalyst, it has to be removed. Traditional method utilizes the controlled surface oxidation. In this investigation two methods namely "Direct Oxygen Oxidation", and "H_2O_2 oxidation" for stabilization of Raney Nickel will be studied.

The main objectives of the study are listed below:

1. Stabilization of Raney - Ni catalyst using conventional controlled surface oxidation, Direct Gas Oxidation, and Hydrogen Peroxide oxidation.

2. Characterization of stabilized catalysts using XRD, SEM, BET surface and Pore size distribution.

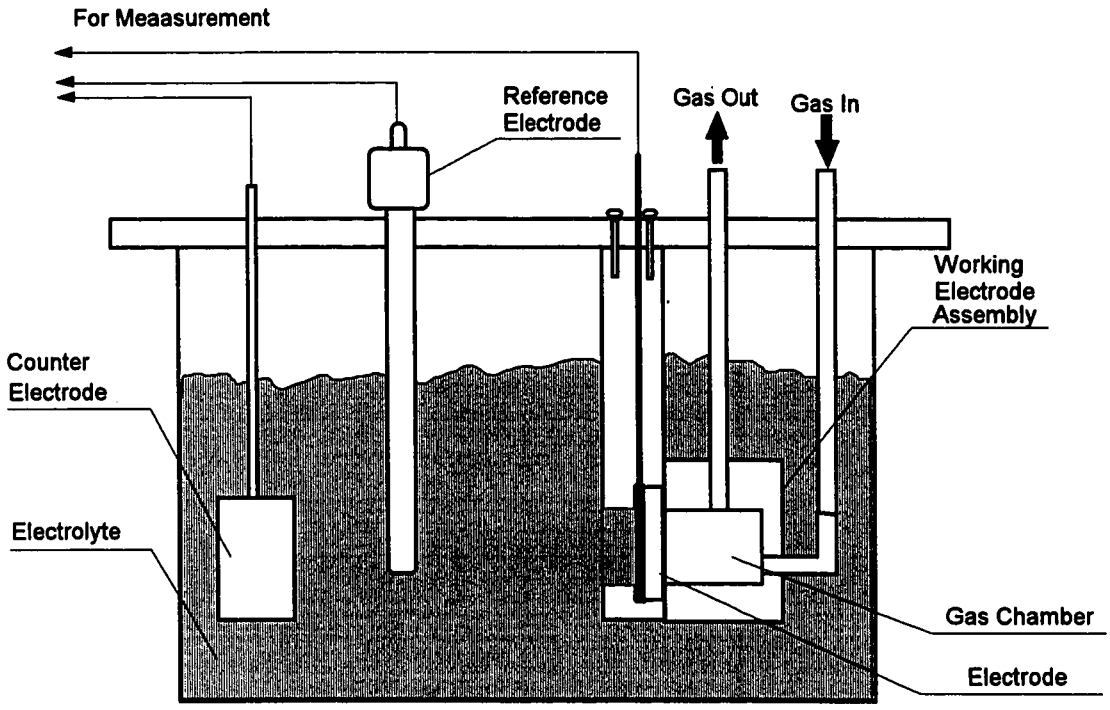


Fig. 1.3: Half cell arrangements

3. Preparation of electrodes using these stabilized catalysts by "Filtration Method"(7).

4. Testing of electrode performance in a half cell set up. Comparison of electrodes performance prepared through various oxidation methods.

5. Reproducibility and long term performance testing of electrodes prepared from a stabilized catalyst by H_2O_2 oxidation.

CHAPTER # 2

Literature Review

In this Chapter available fuel-cell literature has been reviewed. First part discusses the types of the electrocatalyst used for fuel cell anodes. Second part is focused on stabilization of the catalyst. As the catalyst used is pyrophoric, it would overheat when exposed to air. This pyrophoricity can be eliminated by forming an oxide layer of a certain thickness on the surface of the active component. The conventional method utilizes the controlled surface oxidation to form NiO and $Ni(OH)_2$ layer on the catalyst. As it is universal and can be used for all pyrophoric systems, this method is used despite its several disadvantages like accidental overheating of the catalyst, long duration and unstability of the protective layer.

2.1. Electrocatalysts

2.1.1. Requirements of the Fuel-cell Electrocatalysts

A fuel-cell electrocatalyst should posses electronic conductivity, be stable in the fuel-cell environment, and display suitable adsorption characteristics for reactants and/or reaction intermediates. A primary requirement of any electrocatalyst is the stability in the operating environment. For this reason, corrosion testing comprises the first step in the screening process for a candidate electrocatalyst. Corrosion testing usually begins with simple immersion of material in the electrolyte at fuel-cell operating temperature in the presence of the reactant. It is followed by potentiostatic testing in the absence of reactants. Finally long term tests are performed under actual fuel-cell operating conditions. An electrocatalyst must be significantly active. The evaluation of the electrochemical activity is usually done by evaluating the polarization curve for the reaction in the electrolyte of interest on the desired electrocatalyst of well defined composition and surface area. The exchange current density is estimated by extrapolation back to the reversible potential.

To function correctly, an electrocatalytic particle in the porous electrode must be located at a site of electron exchange between the reactants and the products, and must serve as a conduction path way for electrons to current collectors. If the electrocatalyst is a poor

conductor or a semi-conductor, it must be supported or dispersed within a conducting material.

2.1.2. Hydrogen Oxidation Electrocatalysts

The reaction kinetics, mechanism, and modes of electrocatalysis for the hydrogen oxidation reaction are known in considerable details (8,9). The hydrogen oxidation is rapid compared with that for oxygen reduction because it involves only breaking of one single bond, along with two electron transfer steps per molecule. In contrast, oxygen reduction requires the breaking of a double bond and four combined electron-atom transfer steps. In oxygen reduction there is evidence that reaction intermediates are irreversiblly adsorbed because of the affinity of the substrate catalytic species to form a very stable covalent product. In contrast, the hydrogen intermediates are much more reversibly adsorbed, making the desorption reaction much easier.

A. Noble Metal Electrocatalysts

Among the metals that are able to withstand the corrosive conditions in the electrolytes at the appropriate hydrogen potentials, platinum is generally considered to be the most effective electrocatalysts. Other stable noble metals are platinum group metals (gold, silver and mercury), all of which are thermodynamically stable to practical hydrogen electrode potentials. (10). The relative activities for hydrogen reaction in acid electrolyte on clean catalyst surfaces descend in the order:

Platinum, Rhodium> Palladium > Ruthenium >> Gold, WCx (11) Although not entirely unique in its properties as electrocatalyst, platinum does have a combination of properties that promotes electrocatalytic properties. Its vacant d-orbital are such that the metal-reactant bond is neither too strong in which case the reaction products would be unable to desorb, nor too weak which would saturate the surface with intermediates preventing further adsorption of reactants. Under anode reaction conditions platinum does not form oxide layer which would reduce rates for hydrogen activation by blocking sites (12) as they do for oxygen reduction. Platinum has both a good affinity for adsorption of hydrogen atoms, as well as high surface diffusion coefficients (13). In the light of these facts, it can be concluded that although the individual electrocatalytic modalities of platinum are not unique, but they are fortuitously combined in a single material. This has spurred the research for the search of equivalent electrocatalyst. Other noble materials have occasionally been alloyed with platinum for hydrogen reduction. But in general, these metals are not used alone for this purpose.

B. Nickel Electrocatalysts

Although the pure nickel is about three orders of a magnitude less active than platinum for hydrogen electrode processes, it is preferred due to its low cost. The activity can approach to that of noble metals by the use of highest surface area Raney Nickel. Nickel is thermodynamically stable as bulk metal to +110 mV/SHE at pH 14 and 25°C, where as at pH 0 its domain of stability is -550 mV / SHE (10).

This permits its use only in alkaline media. In alkaline media, a reduced nickel oxide layer forms on the metal surface. This layer is capable of adsorbing hydrogen.(14).This is the reason the surface-oxidized nickel is found more active electrocatalytically than the bare nickel. This may be due to an increase in the roughness of the surface on the reduction of oxidized surface.

Sintered nickel alone has been used as an electrocatalyst in alkaline Bacon cell(15) and in molten carbonate fuel-cells. The activity or stability of nickel catalyst is reported (16) to be improved by doping with noble metals (Pt or Pd), cadmium or lead, copper or vanadium, addition of transition metal salts of titanium, maganese, zirconium, vanadium, chromium, tungsten, cobalt and copper to porous nickel hydrogen anodes. The improvement in activity can also be obtained by alloying iron, titanium or molybdenum(13).

C. Miscellaneous Electrocatalyst

Following substances have also been reported to work as electrocatalyst in hydrogen reduction :

Nickel Boride (17)

Mixed Metals (18, 19 20)

$LnM_{4.5-5.5}$ [where ln= La or Sm, M=Ni,Co]

$M_XMn_{3-X}O4$ [where M=Cu,Ni or Ag, x=1-5]

Cu_2Ni_{1-z}, Mn_2O_4 [$z \leq 0.7$]

XY_2O_4[X=Fe, Zn, Mn, Co, Mg, Cd, Cu and Y=Fe, Cr, Mn, Ni or Co]

Tungsten Catalysts

Sodium Tungsten Bronzes (21)

Tungsten Oxide (22)

Tungsten Carbide (23,24)

2.2 Stabilization of pyrophoric Electrocatalysts

The Raney Nickel catalyst, used for fuel cell anodes, is produced by leaching aluminum from Ni-Al alloy in a hot alkali. In this process hydrogen gas evolves and gets adsorbed in the micropores of the Raney-Ni. This makes the catalyst highly pyrophoric as the reaction of adsorbed hydrogen with air liberates considerable amount heat to sinter the catalyst. The pyrophoricity of reduced Raney - Ni catalyst can be eliminated by forming an oxide layer of a certain thickness on the surface of the active component(35) and removing the adsorbed hydrogen(26).

The traditional method for the passivation (stabilization) of pyrophoric catalysts involves prolonged partial oxidation under mild conditions(low partial pressure of oxygen in nitrogen and ambient temperature) to form an oxide layer. Despite its serious disadvantages, viz., long duration, high consumption of pure nitrogen and insufficient stability of the protective layer, this method is used as it is universal and can be used for all virtual pyrophoric systems. The optimal conditions for passivation, i.e., initial concentration of oxygen in nitrogen, duration and degree of oxidation of the metallic component of

the passivated catalysts are specific for each type of catalyst and varying with wide range.

2.2.1 Formation of oxide layer

There are two principle regions of oxygen - nickel interaction that are characterized for pure nickel : A region of direct gas - metal interaction and a region of gas - metal interaction through an oxide layer of certain thickness. The first region corresponds to a rapid exothermic process of metal oxidation. In this region, the process includes the adsorption of oxygen, the formation and growth of nuclei of three dimensional phase of NiO until they overlap, and the formation of a continuous oxide film. The oxide layer thus formed, when it reaches a certain thickness, isolates the metal from direct contact with gas phase but does not prevent further oxidation of metal. When the metal is no longer in direct contact with the oxygen, the process is retorted, then proceeds at a constant decreasing rate (second region), reaching the saturation of the solid phase with oxygen(28).

NiO and $Ni(OH)_2$ formed will increase the electrocatalytic activity considerably. The temperature is kept below 100°C so as to control the oxidation of nickel (25). $Ni(OH)_2$ content of 5 to 6 wt% increases the attainable current density by the factor of 3 - 4. This coating can be produced by careful surface oxidation. This layer can be stabilized by annealing the air oxidized $Ni(OH)_2$ coated catalyst in hydrogen at 350°C, and followed by air oxidation again(26, 27).

Mixture of He + 1% oxygen by volume, and CO_2 is also used for passivation of Ni catalyst. The degree and depth of oxidation of Ni in the catalyst can be characterized for the temperature range of 50 to 250°C, as well as the structure and reproducibility of the oxide layer, The catalyst layer is unstable if the catalysts are heated above the oxidation temperature of the perticular catalyst(28).

2.2.2 Oxidation of the catalyst in the flow of CO_2, water vapor and oxygen

It was found that the pyrophoric characteristics of several industrial catalysts like SA - 1 type (synthesis of ammonia) catalyst, 482 (medium temperature conversion of carbon monoxide), NTK - 4 (lower temperature conversion of carbon monoxide) are rapidly dissipated in a flow of CO_2 in the temperature range of 273 - 823°C. The narrowest range of optimal stabilization temperature can be determine by the nature of the catalyst(29).

Stabilization of some Pyrophoric catalyst in a flow of water vapor or carbon dioxide mixed with water vapor and/or oxygen in the temperature range of -78 to 55°C is studied and proved that apart from the formation of oxide layer, some carbide may also formed. The catalyst stabilized by these methods are sometimes superior to those passivated by traditional methods(30).

2.2.3 High and low temperature stabilization of the catalyst

Low temperature stabilization (-25 to -196°C) or high temperature stabilization (40 to 250°C) can be used for the passivation of pyrophoric catalysts in the flow of air, CO_2 or oxidizing mixtures. These methods provide complete elimination of pyrophoricity(31). The possibility of high temperature stabilization of pyrophoric catalyst by air was checked in the case of catalyst used for the synthesis of ammonia with various chemical composition by varying the size of the catalyst grains and the space velocity of air stream. The results showed that the degree of oxidation of iron at higher temperature does not depend on these parameters(32).

In the case of low temperature stabilization of pyrophoric metal catalysts, it takes 10 to 25 minutes for the stabilization of 13g of the catalyst depending on the air flow rate. The mixture of nitrogen with 0.1% oxygen takes 4 - 6 hr for complete passivation. But catalysts stabilized at high temperature have high resistance to oxidation(33).

2.2.4 Reaction kinetics

The kinetic study reveal that hydrogen is adsorbed on (1 1 1), (1 1 0), (1 0 0) planes of the nickel single crystal. The adsorbed oxygen diffuses in to micropores and reacts with the adsorbed hydrogen. The rate of oxidation on the most densely packed (1 1 1) plane and most loosely packed (1 1 0) planes are similar while the (1 0 0) plane was

oxidized appreciably slower. Initially a rapid chemisorption followed by a slow adsorption occurs before the formation of NiO to a depth of 2 to 3 atomic layers(34). The non homogeneous character of the oxygen sorbed during passivation is due to its weakly bonded adsorbed form. This will result in pyrophoricity of the catalyst(35).

2.2.5 Long term performance

The long term performance and the rate of anodic conversion can be increased by annealing of the slowly air oxidized catalyst samples in hydrogen atmosphere. The aging rate of these annealed catalysts was found to be very small at polarization below the critical value of about 50 mV. The best catalyst can be prepared with the lowest aging rate below 50 μV/h using a titanium doped Raney - Ni with 4 - 6 wt% initial $Ni(OH)_2$ content, which was heat treated in hydrogen atmosphere at 350°C for 5 minutes(36).

Chapter # 3

EXPERIMENTAL SETUP AND PROCEDURE

H_2O_2 treatment method and Direct Gas Oxidation method are studied for stabilization of Raney-Ni catalyst. The experimental setup for these methods along with the conventional method is discussed in this chapter. The stabilized catalyst is used to prepare electrodes by Filtration method(7). Performance of the electrode is tested in a half cell. The setup is also discussed in this chapter.

3.1. Stabilization by Conventional Controlled Surface Oxidation:

The Controlled surface oxidation of Raney-Ni catalyst is discussed in an article by Ewe et. al(41). Fig. 3.1 shows the apparatus used for conventional oxidation. The washed catalyst in a stainless steel plate is placed into a vacuum oven. Vacuum up to 250 to 300 mm bar is maintained. Initially nitrogen gas is introduced to ensure virtually no oxygen is present in the system. The vacuum oven is kept at 60°C.

After careful drying of the catalyst, small amount of air is introduced in to the oven and the temperature is observed. As a result,

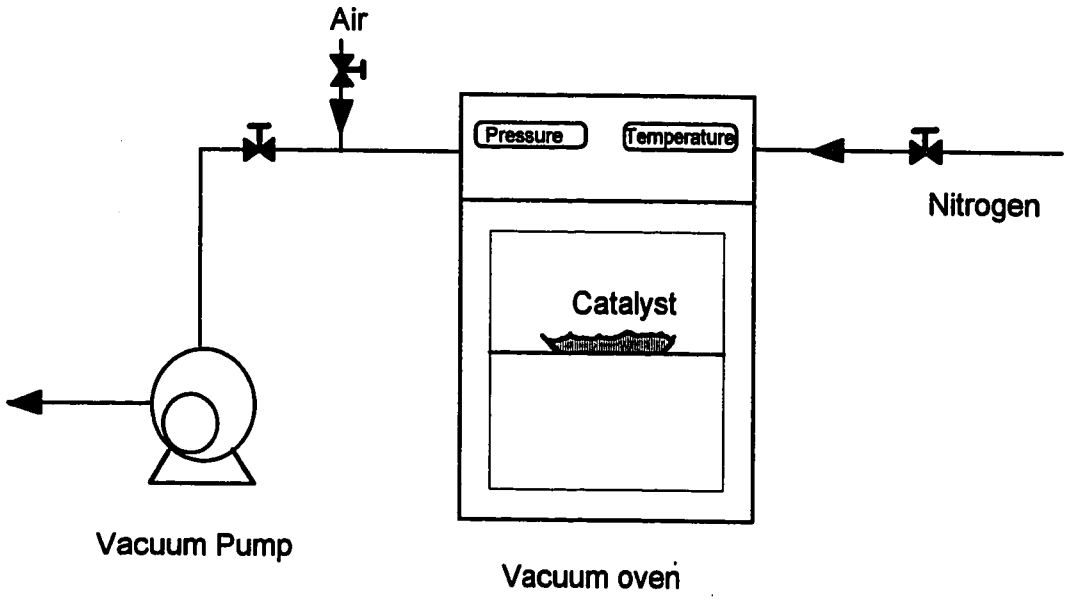


Fig. 3.1: Apparatus for Conventional Controlled Surface oxidation

the adsorbed hydrogen is oxidized to form water. As this reaction is exothermic, it liberates heat. Excess air dose will result in rise in temperature. The sharp increase in temperature may sinter the catalyst. So small doses of air should be introduced carefully in to the system. Nitrogen gas is introduced and vented out several times to dissipate liberated heat. After half an hour another small dose of air introduced and the process is repeated till the oven reaches atmospheric pressure. A small amount of the sample is taken out and tested for pyrophoricity. If there is no visual burning, the catalyst is successfully passivated.

This method is slow, tidious, and involves expensive equipment i.e., vacuum oven, vacuum pump, pure nitrogen. Further, accidental excess passage of air will result in sintering of the catalyst. The H_2O_2 treatment method and Direct Gas Oxidation method are found to be cheap and easy to handle. The experimental setup for these methods is discussed in the forthcoming sections.

3.2. Stabilization by H_2O_2 treatment method:

This method utilizes H_2O_2 to oxidize the nickel catalyst. A batch reactor, used for stabilization, is shown in Fig. 3.2. A known concentration of H_2O_2 is taken in to the reactor. Raney-Ni catalyst of certain weight is added to it and subsequently stirring is started. A vigorous reaction takes place with bubbling and effervescence. The temperature of the reaction is controlled by placing the reactor in ice

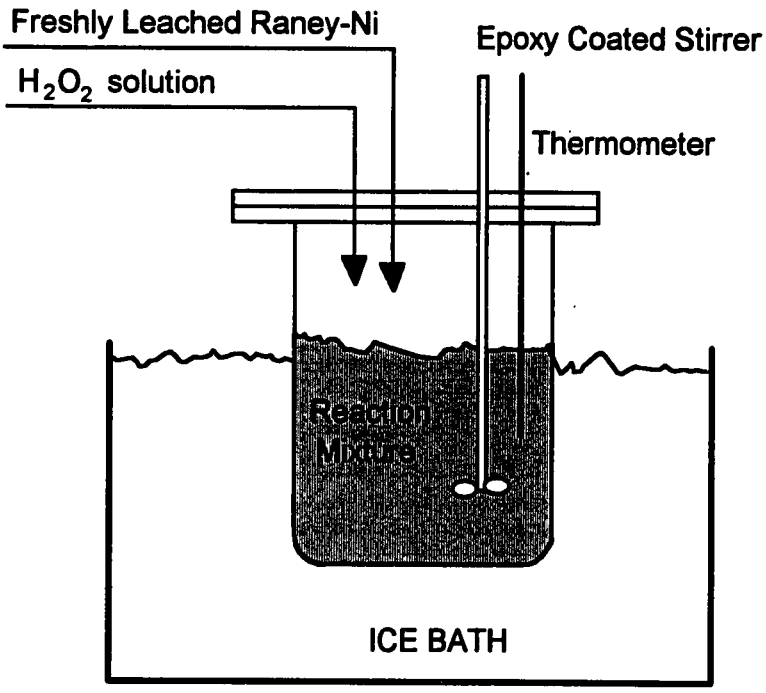


Fig. 3.2: Apparatus for H_2O_2 treatment method

bath. 5, 10, 15, and 25 wt % H_2O_2 are tried for stabilizing the catalyst. For each run, 50 grams. of catalyst is added to 250 ml. of H_2O_2 of certain concentration. The reaction is allowed to go till visible effervescence and bubbling is stopped. The catalyst is dried in vacuum and tested for its pyrophoricity. This method is easy to handle and require no costly equipment.

3.3. Stabilization by Direct Oxygen / Air Oxidation

Another new method of stabilization is much safer and convenient. In this method oxygen is passed into a slurry reactor containing slurry of Raney Ni and distilled water as shown in Fig. 3.3.

Approximately 15 gm of washed catalyst was mixed into 100 gm water. This slurry was decanted into the reactor. The oxygen gas was introduced from the bottom with controlled pressure and flow rate so that the contents of the reactor are not carried over. One sample at the end of each 5 min. was pipetted out and filtered into a Gouch filter (#4). The filter with the catalyst was dried in vacuum. After complete drying the sample was suddenly exposed to the air. The pyrophoric character of these samples was observed visually. First few sample burned immediately. When the adsorbed hydrogen was completely oxidized and a NiO layer of considerable thickness is formed the sample did not burn. When this visual test was conformed, the bubbling of the oxygen was stopped. The catalyst was taken out from the reactor and dried.

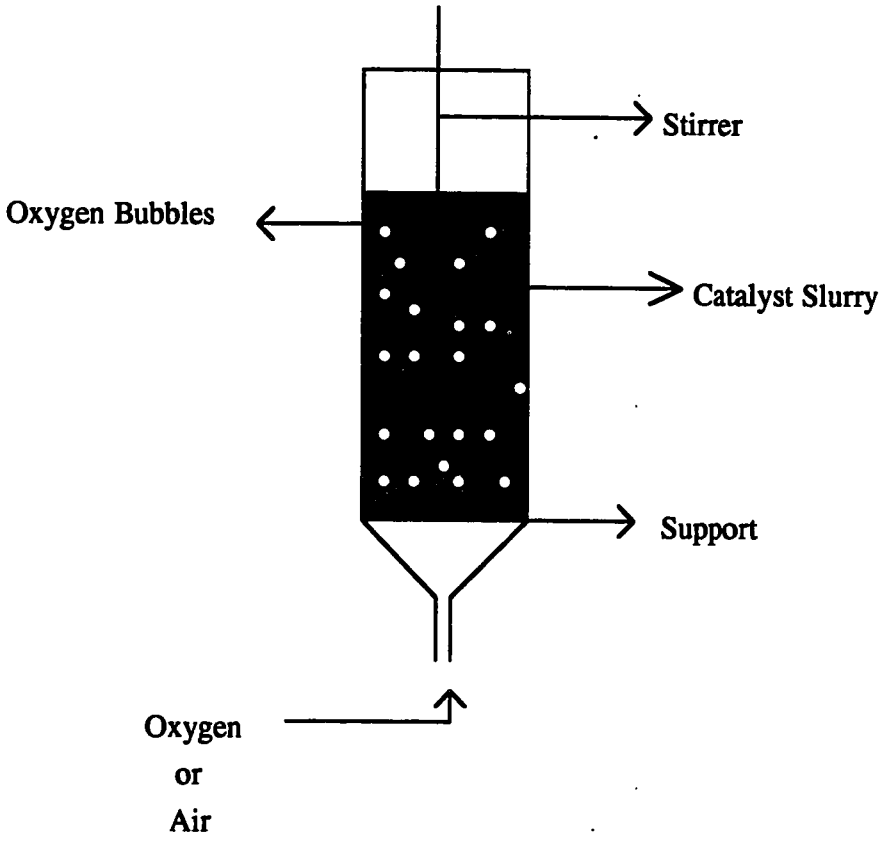


Fig.3.3: Apparatus for Direct Gas Oxidation

3.4 Characterization of the catalysts:

The stabilized catalysts by previous different methods, is characterized to study the structure and active surface of the catalysts. The following techniques have been used for characterization.

1. BET surface area
2. Scanning Electron Microscopy
3. X - ray diffraction
4. Pore Size Distribution

3.5 Preparation of gas diffusion electrodes:

The stabilized catalyst is used to make gas diffusion electrode to test its performance. Filtration method(7) is used to make electrodes. 8 wt.% PTFE powder is added to desired amount of the catalyst to provide hydrophobicity and mechanical strength. This mixture is milled in a high speed mixer to ensure desired bonds. The resulting powder is taken in a household mixer and a surfactant is added to it. Water is poured in to and blended till the powder is dispersed in the solution. The slurry formed is filtered by vacuum filtration as shown in Fig. 3.4. The filter cake formed is dried overnight and rolled on a nickel mesh. The thickness of the electrode is kept at 400 μ. The traces of surfactant present in the electrode is detrimental to its performance. It can be removed by boiling the electrode in acetone for 5 minutes. The resulting washed electrode can be used for performance testing.

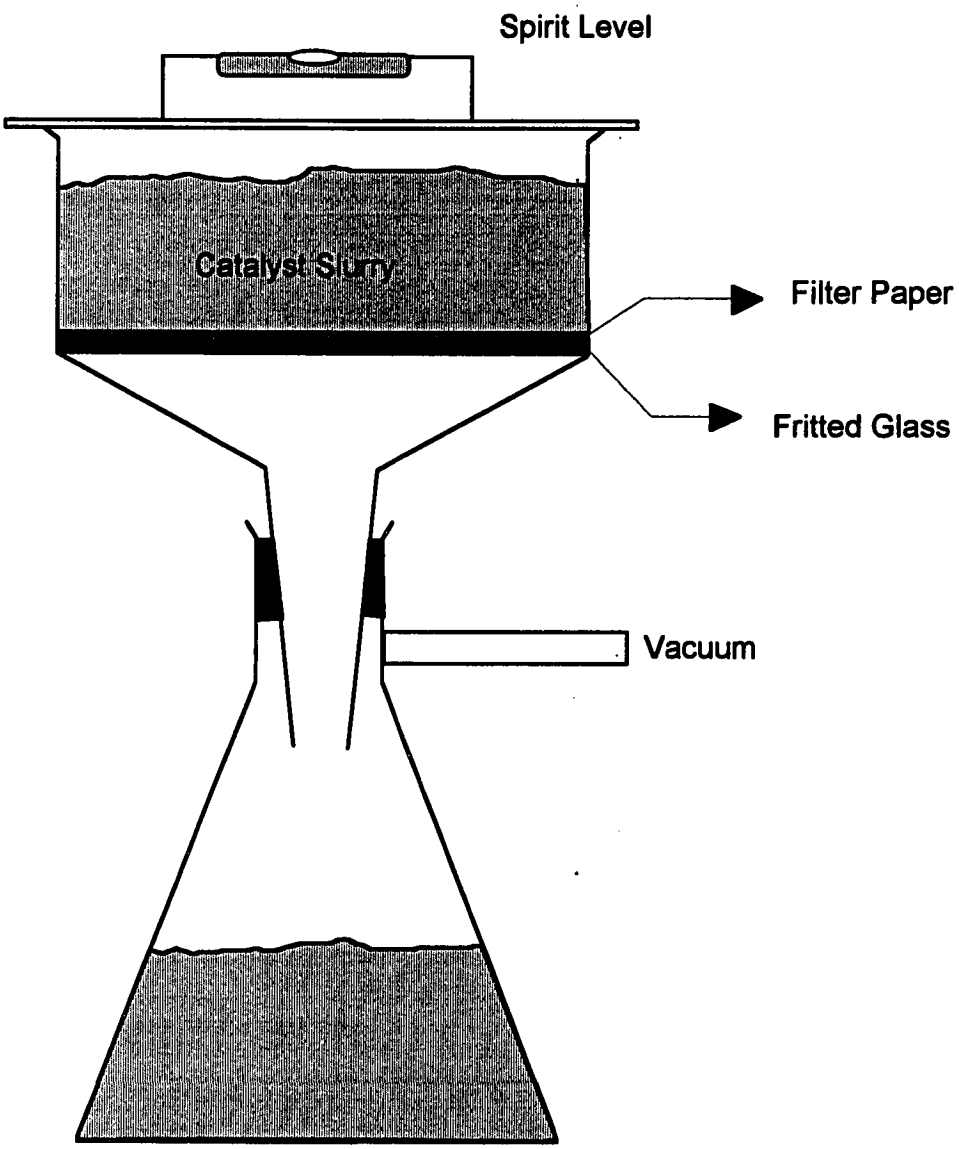


Fig. 3.4: Apparatus for filtration method

3.6. Testing the electrode performance:

Polarization curves for these electrodes are obtained using half cell setup. The half cell setup, procedure for activation of hydrogen electrode and procedure for obtaining the polarization data are discussed in this section.

3.6.1. Half cell Setup:

The half cell consists of two chambers each of which is made of plexi gas. One chamber is used to admit the gas in to the half cell unit and the other chamber is used to hold the electrode between gas and the electrolyte.

Protruding from the electrode chamber are two nickel wires that serve as current collectors from the electrodes. A white Polyteflon fluoro ethane(PTFE) ring acts as a seal against any mixing of the electrolyte and gas. The other accessories include a cylindrical container(about 2 liters volume) with its lid and bolts. 25 wt.% KOH solution is poured in to the cylindrical container till the electrode is completely submerged. A counter electrode, made of nickel foil welded on a nickel rod, is bolted to the plexiglass lid. The reference electrode used is Hg/HgO electrode filled with 25 wt.% KOH solution. This is placed near the working electrode through an opening on the lid of the container. The gas cylinder is connected to the half cell inlet via a regulator, brooks controller and a pressure gauge. The outlet tubing has control valve to apply required back pressure. Fig. 3.5. represents a typical half cell arrangement.

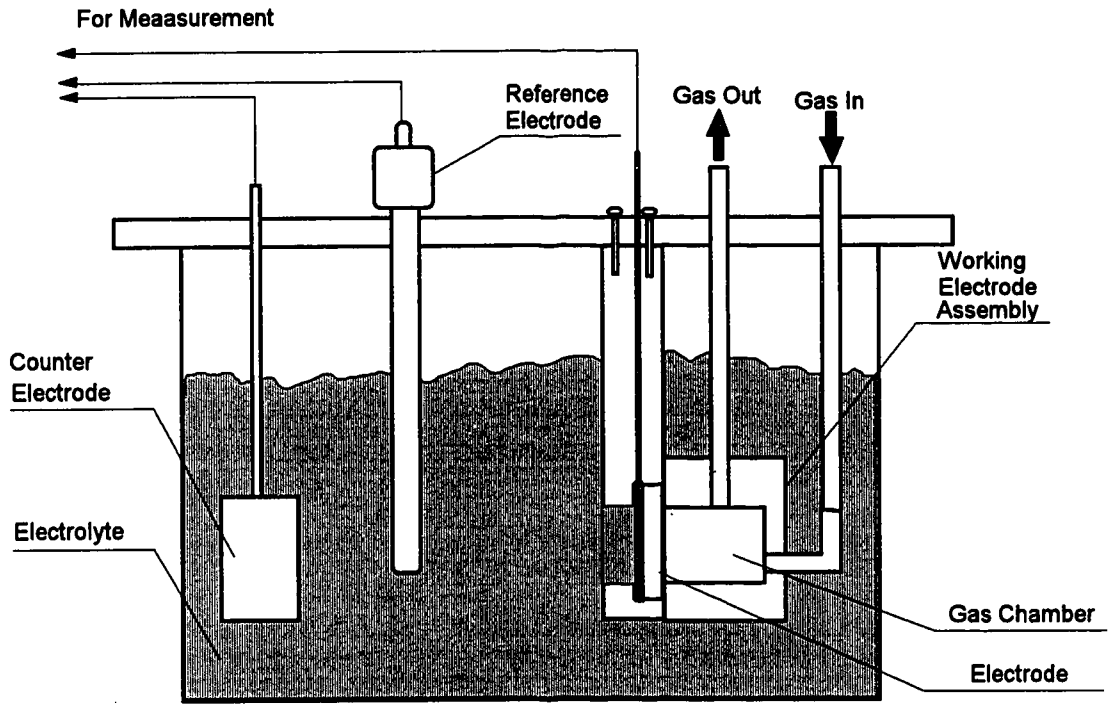


Fig. 3.5: Half cell arrangements

3.6.2. Procedure for Activation and polarization:

I) The potentiostat:

A model-273A, EG & G potentiostat/galvanostat is used for controlling and measuring current and potential of the working electrode in the half cell against a reference electrode (an Hg/HgO electrode) as well as the IR drop in the electrolyte. This equipment has built in IR compensation facility by current interruption method. This equipment can be interfaced to the computer by RS 232-C and IEEE-488(for GPIB).

The microprocessor of the potentiostat recognizes a set of commands which are described in model 273A manual(7). RS 232C or GPIB interface can take commands from the software of the computer. The diagram is shown in Fig. 3.6.

II) IR drop compensation:

IR drop is due to the resistance of the electrolyte present in between working and reference electrodes. The electrode potential read with respect to the respect to the reference electrode incorporates this potential. The actual electrode potential is obtained by subtracting IR drop from this value. Current interruption technique is used to find the IR drop. The current is periodically interrupted and a correction factor is developed based on the potential Vs time change that occurs at the moment of an

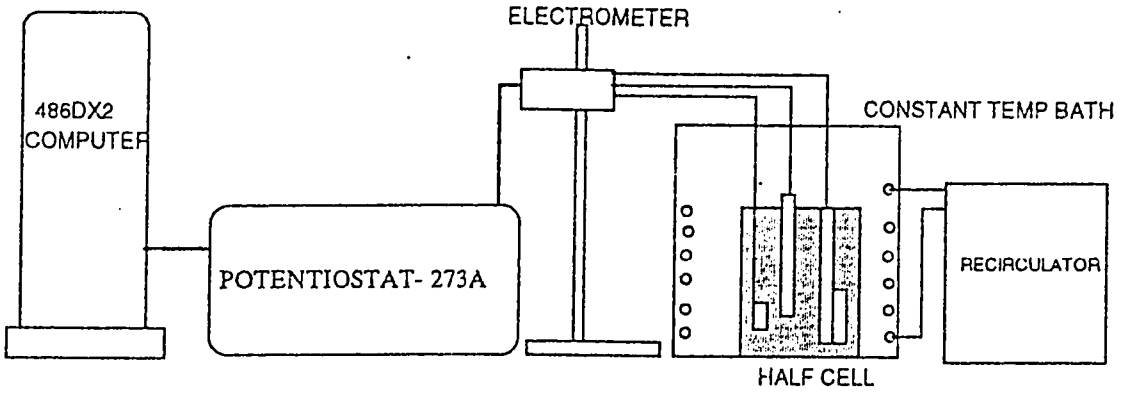


Fig. 3.6: Experimental Setup for Performance testing

interrupt. The current is interrupted in less than 1 second for approximately 190 micro seconds at periodic intervals. When the current interrupts, the potential drops by a value equal to the IR drop. As the interrupts are taking place at different point in time, the IR values at different points in the scan are available.

III) Activation of passivated Raney-Ni electrode:

The passivated electrode was activated by reduction with hydrogen gas while a cathodic current of 25 mA was passed in to the working electrode. The electrode gains its full activity if activation is done for 25 hours at
60°C. The hydrogen gas pressure in the electrode chamber is maintained at 6 psig.

For carrying out the activation, a set of commands was to send to the potentiostat microprocessor. This is performed with the help of a computer program written in 'C'. The program is known as ACTIV. This program generates a file ACTIVE.DAT where the data are stored. An executable file
was made which enables running this program from the DOS prompt. The program is shown in Appendix-A.

After 25 hours, activation is automatically stopped. Then 350 mA anodic current is passed and potential is observed for ten minutes. If the electrode potential is steady, the activation was deemed completed. This is done by a computer program called TEST as shown in Appendix-A.

IV) Polarization of Activated Electrodes.

The polarization data of the activated electrodes in the half-cell assembly were obtained galvanostatically. At one point of time a negative current (anodic) was passed into the cell. The potential of the electrode and the IR-drop was measured for ten minutes. During this time, the system goes to steady state and the potential does not change with time. At this point, the data for the current, potential and IR-drop were obtained. The whole process is repeated for several currents namely 0 ,5 ,10 ,25 ,50 ,100 ,250, 350, 500, 600, 750, 900 and 1000 mA. It is done with a computer program POLA shown in Appendix-A. This program enables the data to store in a file called POLA.DAT. The data from this file are transferred subsequently to LOTUS-123 for plotting.

CHAPTER # 4

Results and Discussion

Controlled surface oxidation, H_2O_2 treatment method and Direct Gas Oxidation method are used for stabilization of pyrophoric Raney-Ni catalyst. The requirements for successful passivation are complete oxidation of adsorbed hydrogen and partial oxidation of Ni surface to enhance the activity of the catalyst by creating the roughness on the surface. This roughness will enhance the adsorption of hydrogen on the catalyst when the actual reaction is taking place in the half cell(36). In the conventional method, 25 mm bar vacuum at 60°C is applied to dry the catalyst(26). After careful drying small doses of oxygen are introduced till the catalyst is completely stabilized. The H_2O_2 treatment method utilizes various concentration of H_2O_2 to react with Raney-Ni. The nascent oxygen liberated in the reaction will react with hydrogen to remove pyrophoricity. The temperature is controlled by an ice bath. The prevailing conditions will also help in partially oxidizing the nickel surface. The maximum reaction temperature when 25 wt.% H_2O_2 is used, reaches about 140°C. This temperature is safe and will not sinter the catalyst. Direct gas oxidation can be done by bubbling oxygen/gas through the slurry of the catalyst.

The dissolved oxygen will diffuse in to the micropores of the catalyst and reacts with hydrogen. Partial oxidation of Ni will take place during passivation. The stabilized catalysts are characterized by XRD, SEM, BET surface and pore size distribution. The performance of the electrodes prepared by these catalysts are tested by polarizing them in a half cell. The observations are tabulated in Table 4.1.

4.1. XRD patterns of Raney-Ni catalyst:

The X-ray diffraction pattern of these catalysts are compared to the standard Ni, NiO, and $Ni(OH)_2$ peaks to know their presence and crystalinity of the sample. As there is no peak corresponding to $Ni(OH)_2$,indecating its absence in the samples.

Fig. 4.1 is the XRD pattern of conventionally stabilized catalyst. The sharp peaks represents the crystalinity of the catalyst. The peaks corresponding to standard NiO pattern signifies its presence in the sample. Fig. 4.2 shows the XRD patterns of 5, 10 15, and 25 wt.% H_2O_2 stabilized catalysts. For all the cases the XRD pattern is more or less the same. The NiO content in stabilized catalysts is found by EDS. spectra. As this method gives the NiO content at a particular point of the sample, this data is not reliable. Nevertheless, the results are tabulated in Table. 4.2. Fig. 4.3 represents the XRD pattern of the catalysts stabilized by Direct Gas Oxidation, inferring that these catalysts are also crystalline with considerable NiO content.

TABLE 4.1: Experimetal conditions and observations

Run #	Type of stabilization	Reaction Temperature	Pressure	Time for Stabilization
1	Conventional	60°C	250 mm bar	>12 hr.
2	5 wt.% H_2O_2	35 - 40°C	Atm.	15 min.
3	10 wt.% H_2O_2	45 - 55°C	Atm.	15 min.
4	15 wt.% H_2O_2	50 - 75°C	Atm.	15 min.
5	25 wt.% H_2O_2	70 - 110°C	Atm.	15 min.
6	Low flow rate Oxygen	30 - 40°C	10 psig	30 - -40 min.
7	High flow rate Oxygen	30 - 40°C	20 psig	30 - 40 min.
8	Air	30 - 40°C	20 psig	60 min.

TABLE 4.2: NiO content of Stabilized catalysts

Type of Stabilization	NiO content, wt%
Conventional	4
5% H_2O_2	5
10% H_2O_2	6
15% H_2O_2	15
25% H_2O_2	16
Low Flow Rate O_2	8
High Flow Rate O_2	8
Air	7

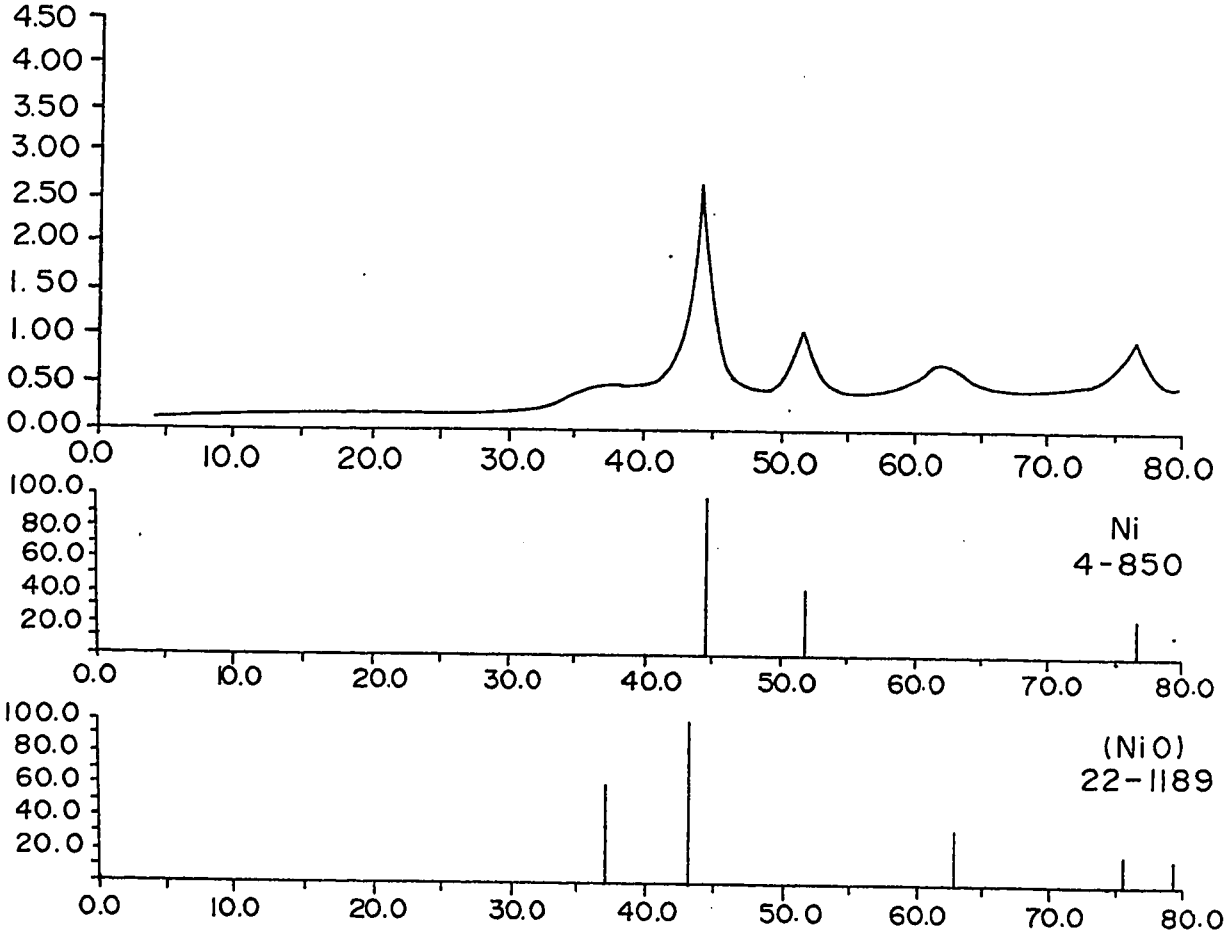


Fig. 4.1: XRD pattern of conventionally stabilized catalyst

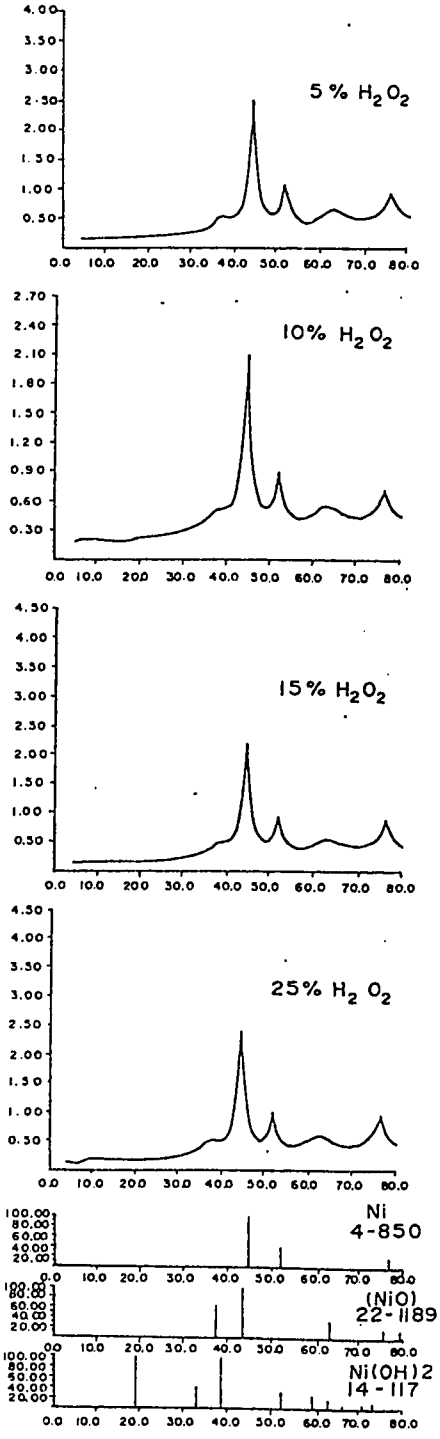


Fig. 4.2 : XRD patterns of 5, 10, 15, 25 wt.% H2O2 stabilized catalysts

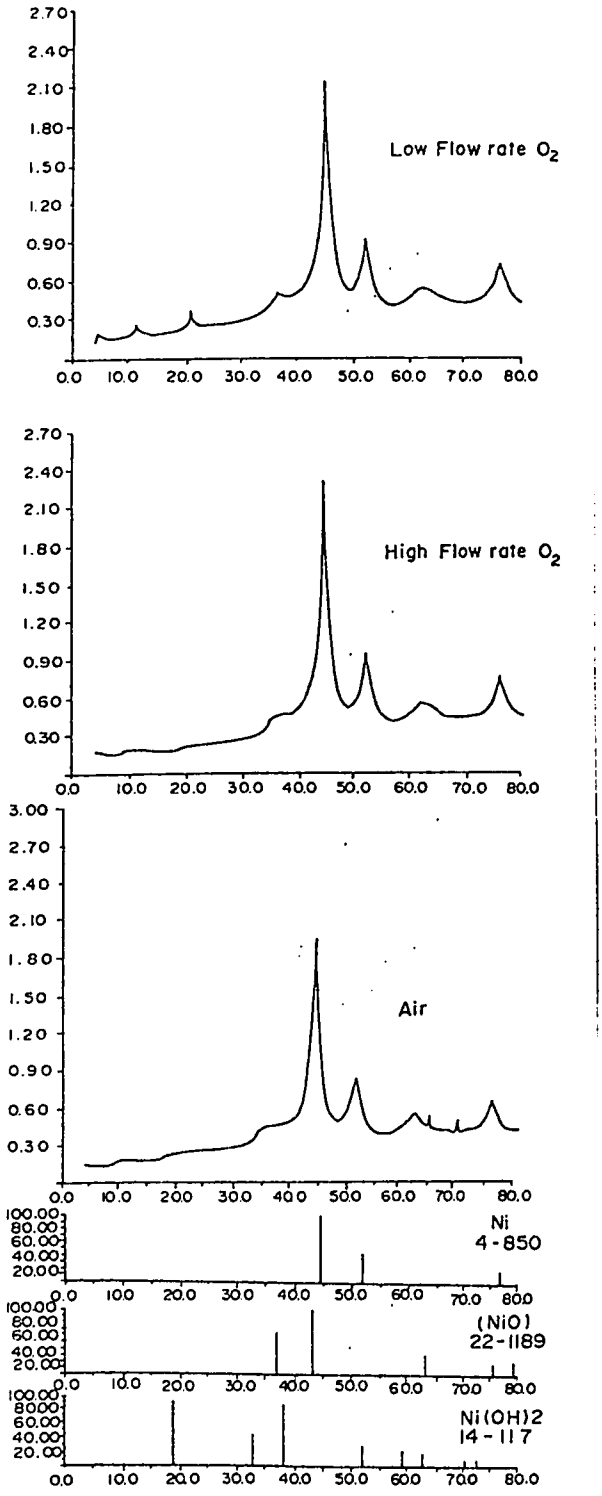


Fig. 4.3 : XRD patterns of Direct Gas Oxidation catalysts

This section concludes that all catalysts contain crystalline Ni and considerable NiO content.

4.2. Scanning Electron Micrograph of the Raney-Ni catalyst:

The SEMs gives the surface morphology of the catalyst. A 5000 magnification of catalysts stabilized by various methods are shown in Fig. 4.4, 4.5(a),(b) and 4.6. The particles are regular in shape and have different sizes varying from sub microns to 500 μ. These SEMs show that the particles have sharp edges and are not diffused in to one another suggesting no appreciable sintering of the catalyst. The pore size distribution of all samples are shown in Fig. 4.7 and 4.8. Most of the particles are of average size 150 μ. The higher the pore size, the lesser will be the surface area and less active will the catalyst be, In all cases the pore size distribution is more or less the same or comparable except for 5% H_2O_2 stabilized catalyst and low flow rate oxygen stabilized catalyst. The reason for the variation of pore size distribution of these two catalysts is insufficient oxygen content and unstable NiO layer formed during stabilization.

This section concludes that, the newly developed methods are comparable to the traditional method. These catalysts can be used for making electrodes since there is no apparent sintering of the catalyst.

Fig. 4.4: Scanning Electron Micrograph of Conventionally stabilized catalyst

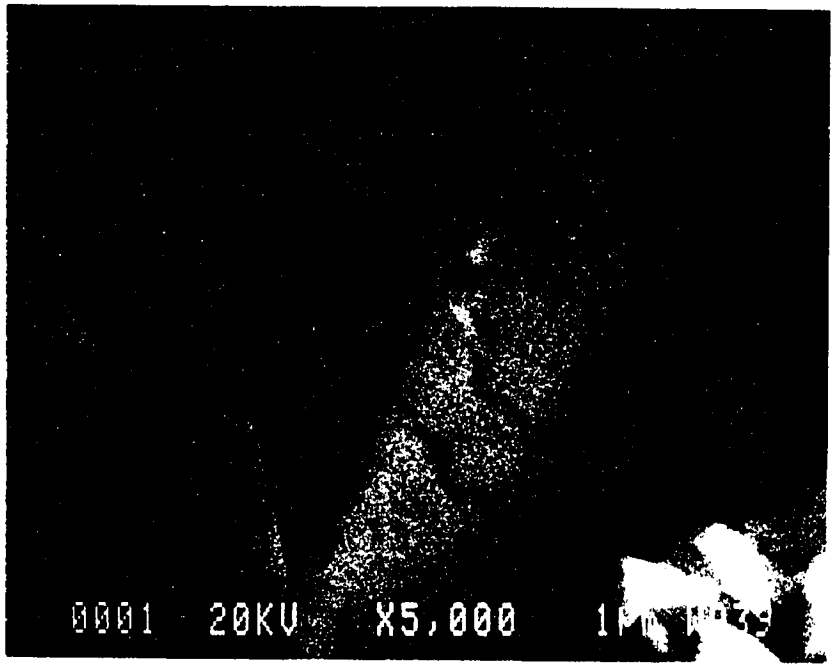


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Fig. 4.5(a): SEMs of 5, 10 wt.% H_2O_2 stabilized catalysts

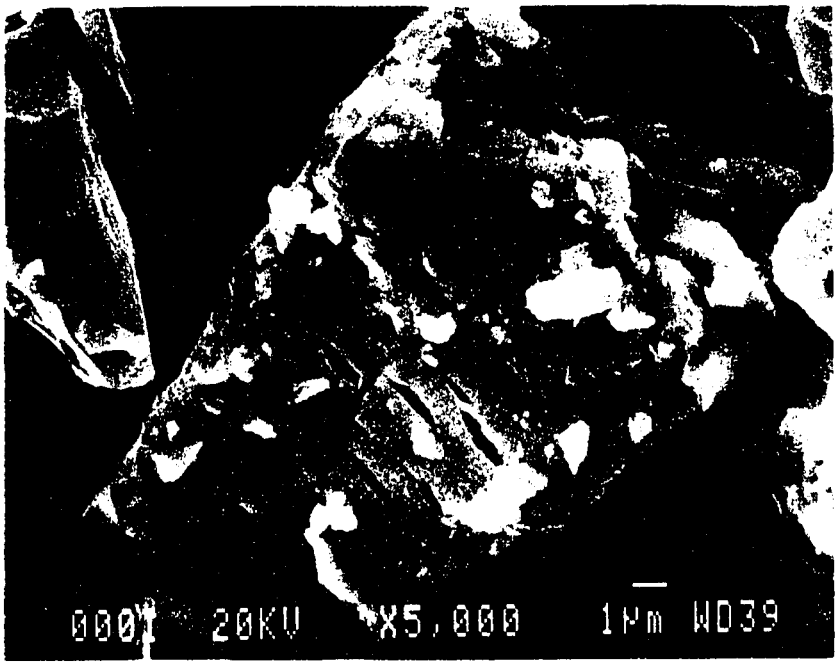

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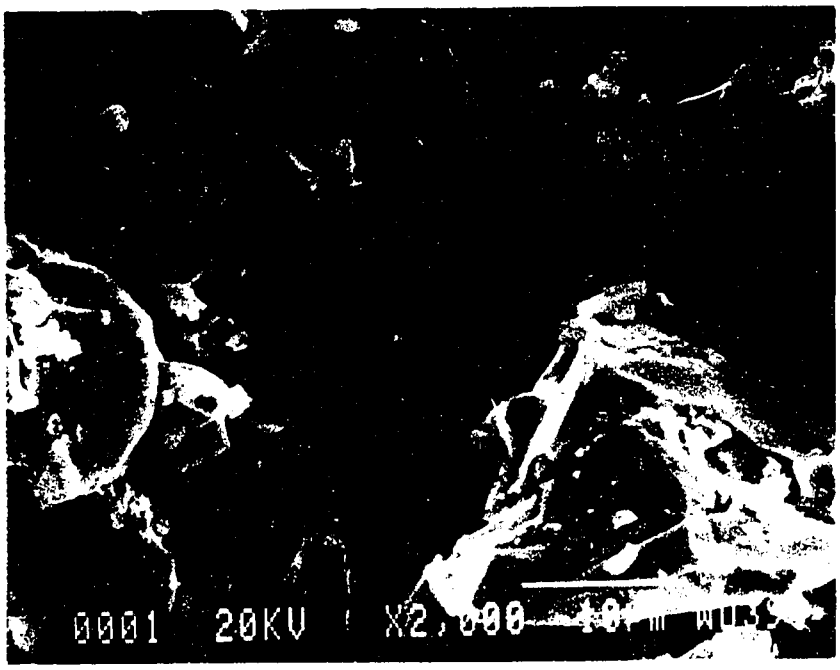
Fig. 4.5(b): SEMs of 15, 25 wt.% H_2O_2 stabilized catalysts



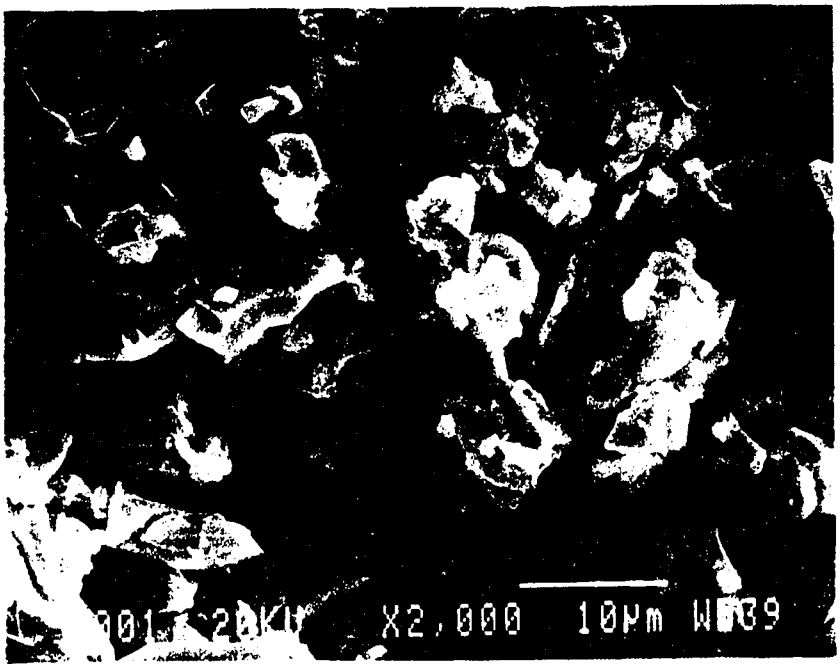


Fig. 4.6: SEMs of Gas stabilized catalysts

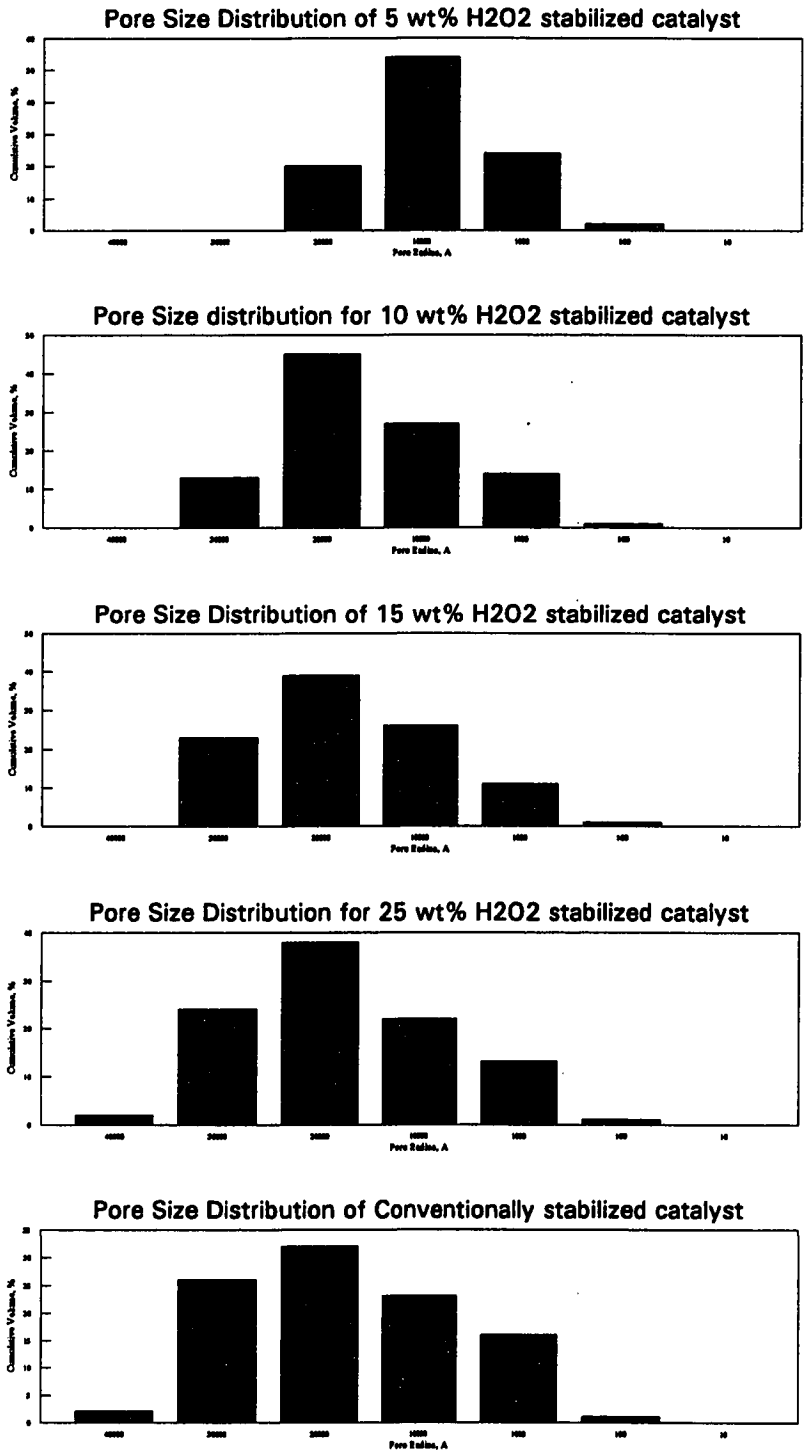


Fig. 4.7: PSD of Conventional and H_2O_2 stabilized catalysts

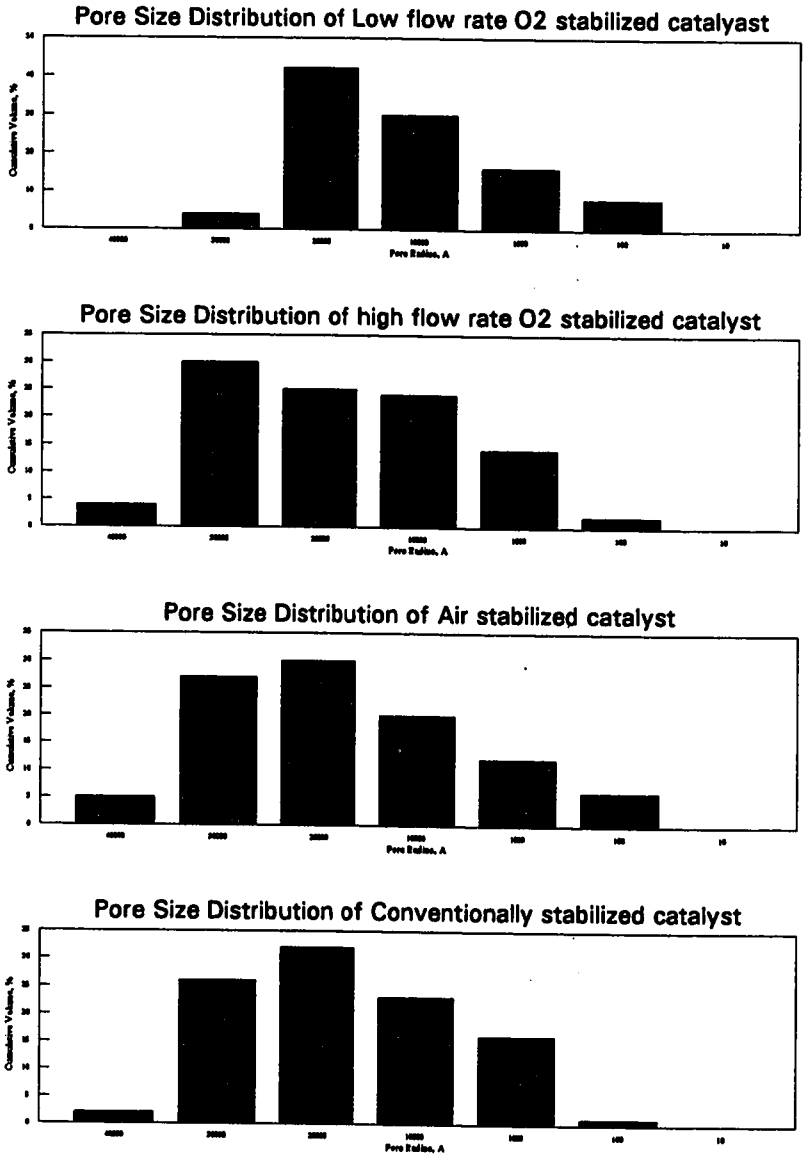


Fig. 4.8: PSD of Conventional and Gas stabilized catalysts

4.3. BET surface:

The BET surface represents the total active area of the catalyst for any reaction to take place. The data for various stabilized catalysts is tabulated in table 4.3.

15 wt.% and 25 wt.% H_2O_2 stabilized catalysts have higher surface area compared to the catalysts stabilized by conventional and direct gas oxidation methods which represents the high activity of high concentration H_2O_2 stabilized catalysts. The reason for the lesser surface area of the 5 and 10 wt.% of H_2O_2 stabilized catalysts is insufficient oxygen content to remove hydrogen and partially oxidize the catalyst. Further more the optimum temperature for stabilization of the catalyst is 60 to 90°C(26).This will successfully remove the adsorbed hydrogen and partially oxidizes the catalyst.In the case of less concentrated H_2O_2 stabilized catalysts, the reaction temperature reaches only 40 to 50°C. The reaction temperature in Direct Gas Oxidation method reached only up to 40°C then droped down because of the adiabatic expansion of gas from the cylinder. The weakly bonded oxygen may not be enough for sufficient oxidation of hydrogen as well the Ni catalyst.

The characterization techniques showed that the three methods for stabilization are successful in passivating the catalyst and forming the NiO layer on the surface. As the stability, percentage of NiO coating and extent of oxidation of hydrogen may not be the same in all

TABLE 4.3: BET surface of stabilized catalysts

Type of Stabilization	BET surface, m^2/g
Conventional	51
5% H_2O_2	35
10% H_2O_2	48
15% H_2O_2	65
25% H_2O_2	63
Low Flow Rate O_2	18
High Flow Rate O_2	19
Air	16
Sintered catalyst	9

cases and their performances may differ. Electrodes are prepared using these catalysts and tested for their performance.

4.4. Performance testing of the electrodes:

The catalysts stabilized by different methods are mixed with PTFE powder and rolled on nickel mesh to make electrodes. Filtration method (7) is used for making electrodes. This method was discussed briefly in chapter 3. The polarization data for all electrodes is given in Appendix. D. Over Potential Vs current density is plotted for each electrode. Fig. 4.9 compares the performance of H_2O_2 stabilized electrode to the conventional electrode. 15 and 25 wt.% H_2O_2 stabilized electrodes have better performance than conventional electrode. One of the reason for this is their higher BET surface area as in table 4.3. the other reason may be the stable NiO present in these H_2O_2 stabilized catalyst. The higher NiO content shown in table 4.2 will support this result. As far as 5 and 10 wt.% H_2O_2 stabilized catalysts are concerned, the reaction temperature is around 50°C and the nascent oxygen liberated by H_2O_2 may not be sufficient to oxidize hydrogen and the catalyst. This will result in low BET surface, low NiO content and insufficient passivation which will result in poor performance.

Over potential Vs concentration of H_2O_2 plotted at various current densities are shown in Fig. 4.10. Initially, the over potential is decreasing with increase in concentration till 15 wt.% H_2O_2 and no

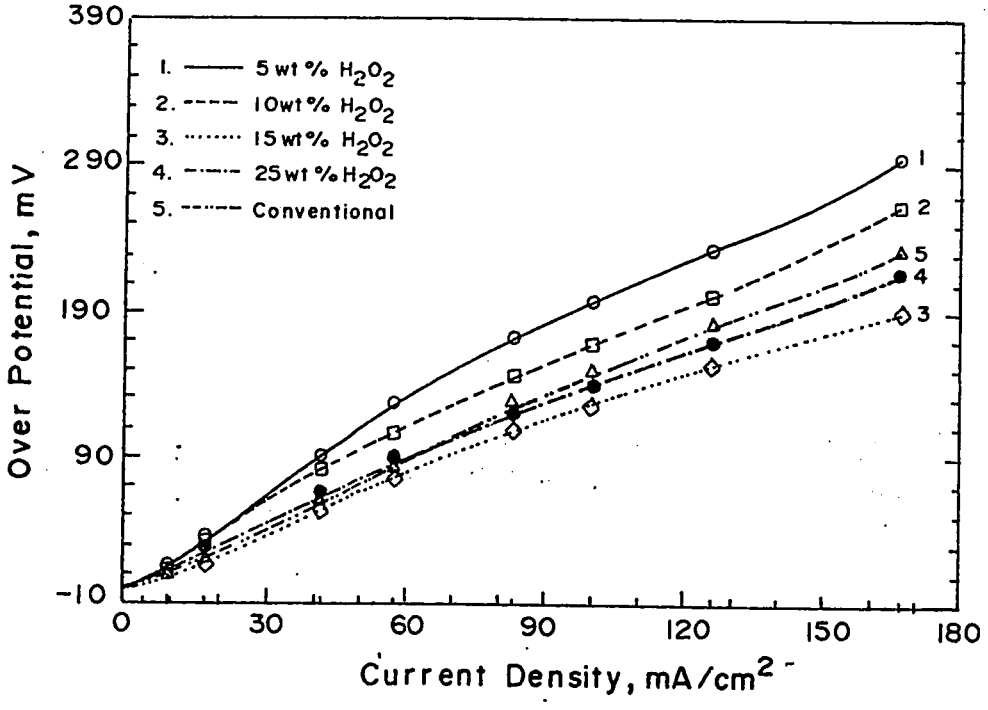


Fig. 4.9: Comparison of performance of H_2O_2 stabilized electrodes to conventionally stabilized electrodes

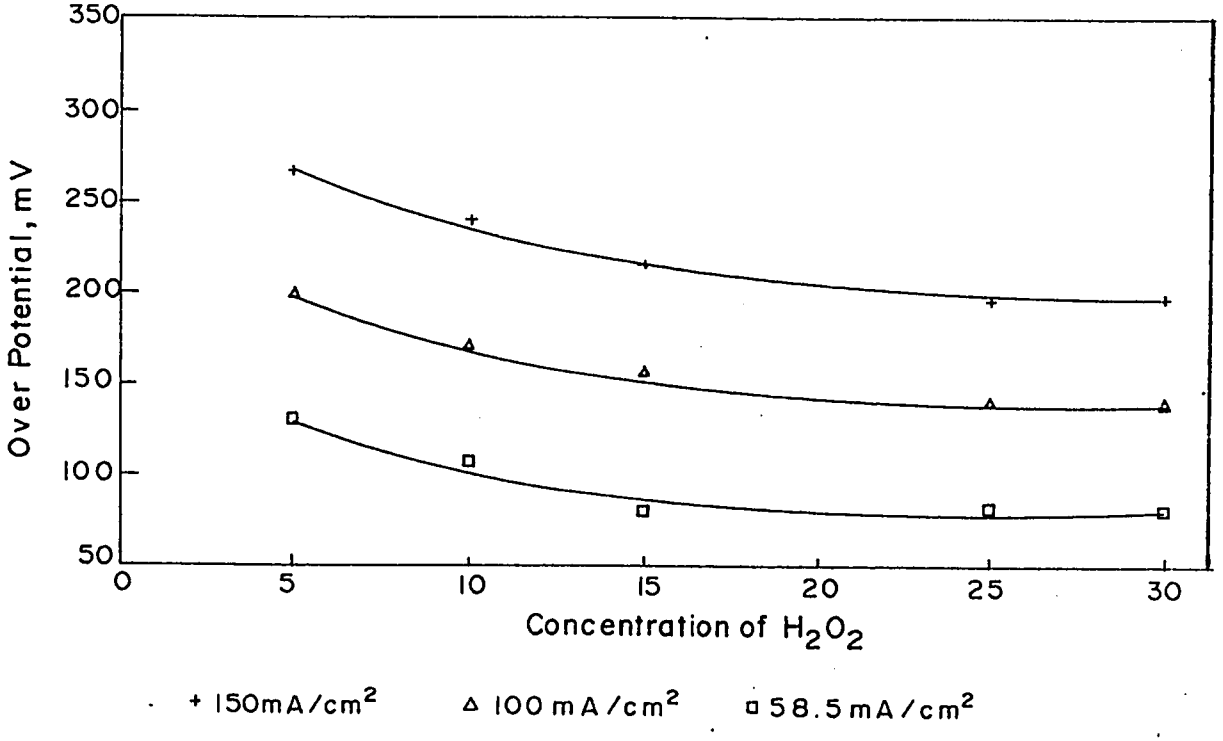


Fig. 4.10: Concentration of H_2O_2 Vs Over Potential at different current densities

change is observed further. This concludes that 15 wt.% H_2O_2 is sufficient and rather economical for successfully passivating the catalyst.

Fig. 4.11 compares the performance of Direct Gas Oxidation electrodes to conventional electrodes. It represents that the performance of these newly prepared electrodes are some what poor compared to conventional electrodes. This is because of the reaction temperature of direct gas oxidation method. As mentioned earlier, 60°C is the optimum for passivation and since the reaction temperature is only around 40°C, the passivation is not effective and the NiO formed is not stable. This results in lesser activity of the catalyst and thereby lesser performance. Table 4.2 and 4.3 support these results. Nevertheless, further studies could be done by keeping the temperature of the slurry at around 60°C. This may result in highly active catalyst.

4.5.1 Long term performance and reproducibility of 15 wt.% H_2O_2 stabilized electrode:

As 15 wt.% H_2O_2 stabilized electrode has higher performance than conventional electrode, further studies have been done to find its long term performance and reproducibility. At 100 mA/cm^2 cathodic current density and 25°C, the electrode is kept for 170 hours and found no significant loss in voltage. The comparison of long term performance tests of this electrode to conventional electrode is shown in Fig. 4.12. A fresh sample of leached catalyst is taken again and

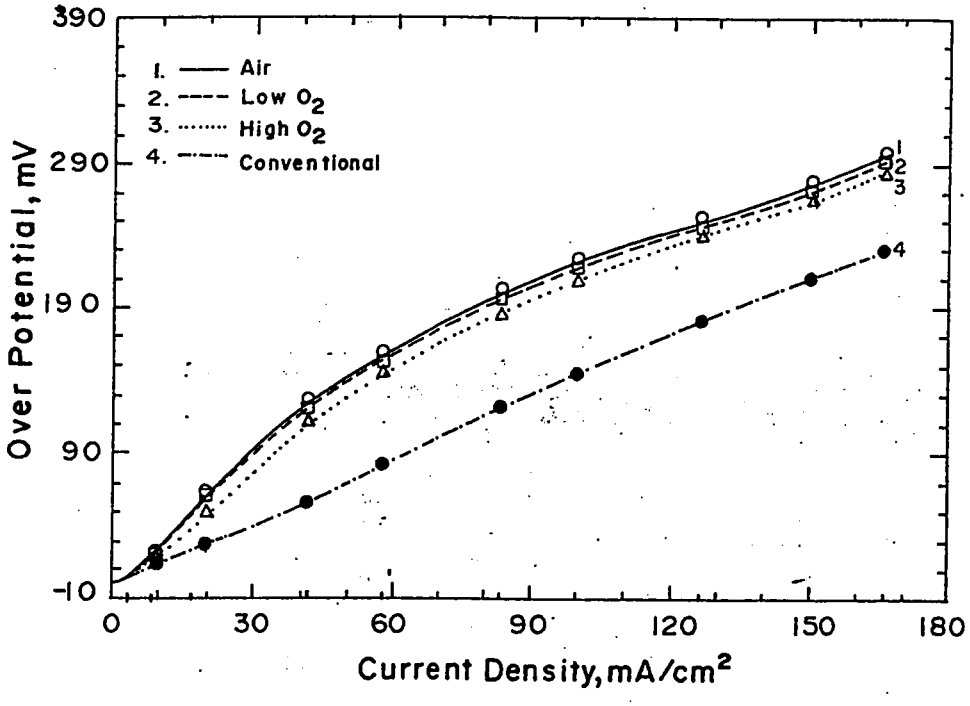


Fig. 4.11: Comparison of performance of Gas stabilized electrodes to conventionally stabilized electrodes

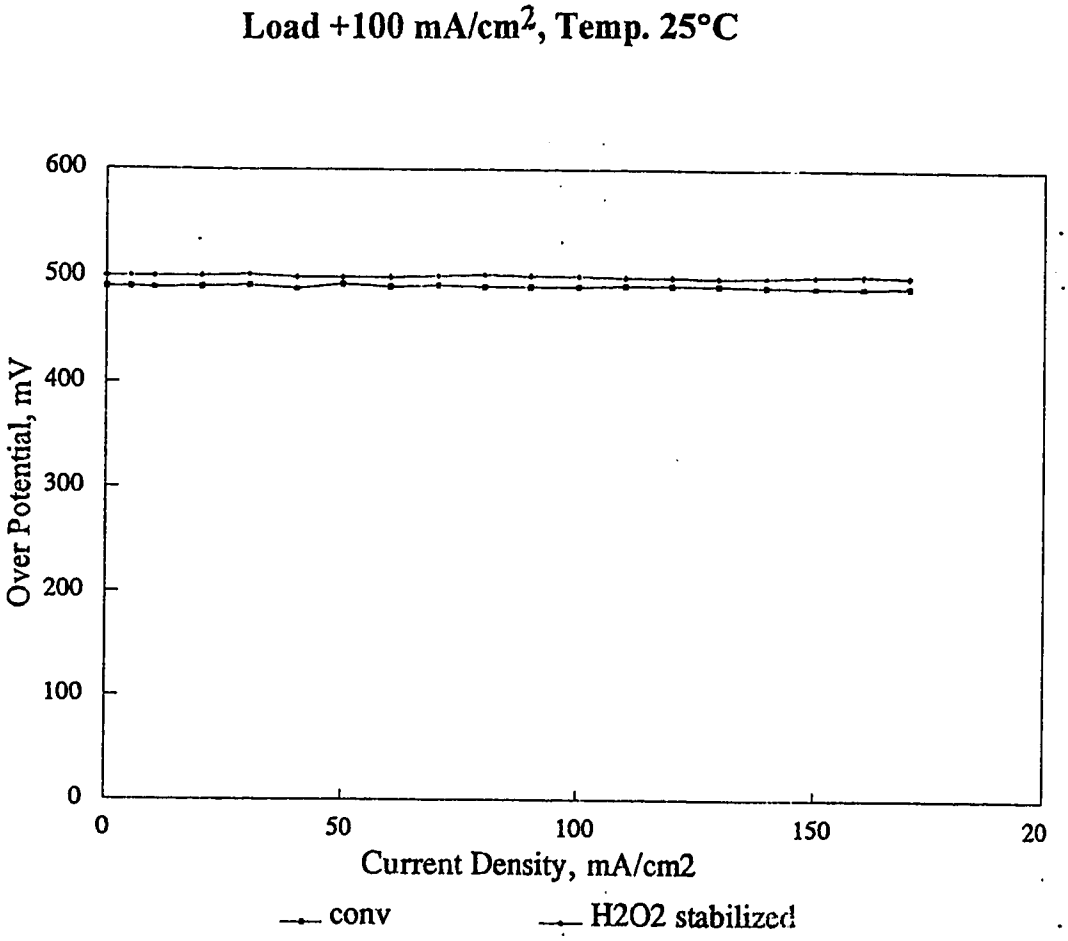


Fig. 4.12: Long term performance of H_2O_2 stabilized electrode to conventional electrode

reacted with 15 wt.% H_2O_2 to test for its reproducibility. Table 4.4 shows that the electrode is reproducible since there is no apparent change in its performance.

4.5.2 Exchange current density and transfer coefficients of the electrodes.

The general form of the current density - Over Potential relation for a multi electron transfer reaction(38) is

$$i = i_0(Exp(^{\alpha\eta F}/_{RT}) - Exp(^{-(1-\alpha)\eta F}/_{RT})) \qquad (4.1)$$

where α is the transfer coefficient of the reaction. This equation is known as Butler - Volmer equation.

At lower over potentials Eq. 1 reduced to

$$\eta = \frac{RT}{F}\frac{i}{i_0} \qquad (4.2)$$

For lower current densities of up to 42 mA/cm^2, η Vs i were plotted in Fig. 4.13 using Eq. 4.2. It shows that this relation for lower current densities

is linear. Exchange current densities are found using the slope of the stright line. For various electrodes, exchange current densites are found and tabulated in Table 4.5. It can be noted that the exchange current density for a 15 wt% H_2O_2 stabilized electrode is better compared to other electrodes. These results are in consent with the charecterization and performance tesitng results.

TABLE 4.4: Reproducibility of H_2O_2 stabilized electrode

Current Density, mA/cm^2	Over Potential, mV		Difference
	run # 1	run # 2	
0	0	0	0
0.83	0	0	0
1.83	0	0	0
4.33	1	1	0
8.33	6	7	-1
16.67	17	19	-2
41.83	54	52	2
58.33	76	78	-2
83.33	110	117	-7
100.16	131	138	-7
125.00	156	162	-6
150.00	176	183	-7
166.67	192	198	-6

TABLE 4.5: Exchange current densities of various electrodes at lower over potentials using Eq. 4.2.

Type of stabilization	Slope	$i_0.10^3$ mA/cm^2
Conventional	0.72782	18.81
5 wt.% H_2O_2	0.526565	12.28
10 wt.% H_2O_2	0.56812	12.49
15 wt.% H_2O_2	0.802	20.73
25 wt.% H_2O_2	0.69674	18.01
Low O_2 flow rate	0.34478	8.91
High O_2 flow rate	0.39627	10.24
Air	0.3326	8.5965

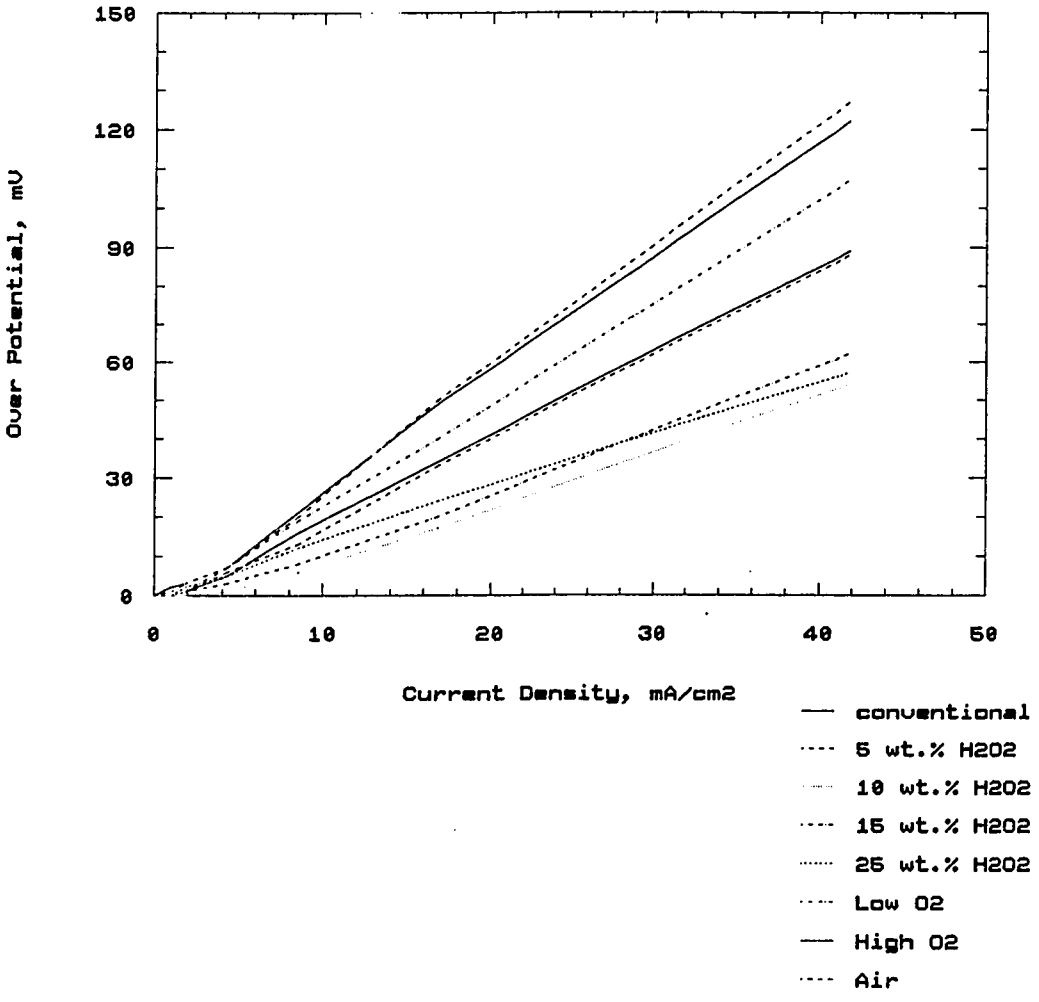


Fig. 4.13: Current Density Vs Over Potential at lower over potentials

4.5.3 Dependence of current density on H_2O_2 concentration at constant over potentials

At a particular over potential, current density Vs concentration of H_2O_2 data is plotted. A second degree polynomial is fitted (eqn.3) to the data and parameters are found using STATGRAF package.

$$I = a + b\,C_A + c\,C_A^2 \qquad (4.3)$$

Where I is in mA/cm^2 and C_A in wt.%. The parameters are tabulated in Table 4.6

4.5.4 Dependence of current density on Oxygen partial pressure at constant over potential

At a given over potential, Current Density Vs oxygen partial pressure is plotted and a higher degree polynomial is fitted accordingly. Eq. 4 represents their relation.

The parameters are tabulated in Table 4.7.

$$I = a + b\,P_{o_2} + c\,P_{o_2}^2 \qquad (4.4)$$

Where I is in mA/cm^2 and P_{o_2} in psi.

TABLE 4.6: Parameters of current density Vs concentration of H_2O_2 data

η, mV	a	b	c
90	25.38	2.96	-0.01872
130	27.6688	6.5447	-0.022665
190	56.2956	7.83	-0.01789

TABLE 4.7: Parameters of current density Vs Oxygen partial pressure data

η, mV	a	b	c
90	27.7675	0.2848	0.01347
130	43.7675	0.2849	0.01347
190	77.5411	0.018836	1.204258

CHAPTER # 5

Conclusions and Recommendations

5.1 Conclusions

1) H_2O_2 treatment method and Direct Gas Oxidation method are found to be successful in stabilizing the pyrophoric Raney -Ni catalyst as compared to Conventional controlled surface oxidation method.

2) 15 wt.% H_2O_2 concentration is found to be optimum for stabilizing the Raney-Ni catalyst. The electrode prepared from this catalyst has shown better performance compared to conventional electrode.

3) Direct Gas Oxidation electrodes have shown poor performance as compared to the conventional electrode because of unstable NiO, low BET surface and high over potentials.

4) Long term performance tests for the electrode prepared from the catalyst stabilized by 15 wt% H_2O_2 showed that a 170 hr operation

at 100 mA/cm^2 cathodic current density will not deactivate the catalyst.

5) Reproducibility test for the electrode prepared from the catalyst stabilized by 15 wt% H_2O_2 showed that they are reproducible.

5.2 Recommendations

1) Modeling of slurry reactor for Direct Gas Oxidation has to be done to calculate the optimum parameters such as space time of gas, reaction time etc.,

2) Direct Gas Oxidation method should be modified by maintaining constant temperature in the slurry reactor.

3) Optimum value of catalyst loading need to be known.

4) Performance testing of Raney - Ag for alkaline fuel cell cathodes has to be done.

5) The complete fuel cell using Raney - Ni and Raney - Ag electrodes should be fabricated.

6) Annealing of stabilized catalyst should be done to stabilize NiO and $Ni(OH)_2$ layers which will increase the performance of electrode.

7) Long term performance of the electrodes for more than 1000 hr. should be studied.

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APPENDICES

APPENDIX - A

('C' Programs to run Half Cell experiments)

```
**********************************************************
```

'C' program to run activation experiment
Program name: ACTIV

```
**********************************************************

#include <bios.h>
#include <stdio.h>
#define  DATA_READY 0x0100;

unsigned int _bios_serialcom(unsigned int, unsigned int, unsigned int);
void main()
{

FILE *fpw;      /*pointer for the write file*/

char command1[]="DCL;SIE 15;CELL 1;MODE 1;S/P 6000;TMB 50000\n";
char *ptr1 ;
char command2[]="PAM 1;IRMODE 3;SETI 25 -3;DO
150;TP;RUERR;LOOP\n";
char *ptr2 ;
char command3[]="DO 150;TP;RUERR;LOOP\n";
char *ptr3 ;
char command4[]="CELL 0\n";
char *ptr4 ;
unsigned int r;
unsigned int com_status;
int i;
   fpw=fopen("aCTIV.dat","w");
   ptr1=command1;
   ptr2=command2;
   ptr3=command3;
   ptr4=command4;
   com_status=_bios_serialcom(_COM_STATUS,1,0);
   printf("COM2 Status:0x% .4x \n", com_status);
   _bios_serialcom(_COM_INIT,1,_COM_CHR8 |
                           _COM_STOP1 | _COM_NOPARITY |
                           _COM_300);
```

```
 while (*ptr1 != NULL) {
_bios_serialcom(_COM_SEND,1,*ptr1);
 ptr1++;
}


i=0;
r=' ';
while(r  != '*') {
   com_status= _bios_serialcom(_COM_STATUS,1,0);
   printf("COM2 Status:0x% .4x \n", com_status);

      r=_bios_serialcom(_COM_RECEIVE,1,0);
  fwrite(&r,1,1,fpw);


}
while (*ptr2 != NULL) {
_bios_serialcom(_COM_SEND,1,*ptr2);
 ptr2++;
}


 r=' ';
while(r  != '*') {
   com_status= _bios_serialcom(_COM_STATUS,1,0);
   printf("COM2 Status:0x% .4x \n", com_status);

      r=_bios_serialcom(_COM_RECEIVE,1,0);
  fwrite(&r,1,1,fpw);


}
while (*ptr3 != NULL) {
_bios_serialcom(_COM_SEND,1,*ptr3);
 ptr3++;
}


 r=' ';
while(r  != '*') {
   com_status= _bios_serialcom(_COM_STATUS,1,0);
```

```
    printf("COM2 Status:0x% .4x \n", com_status);

       r=_bios_serialcom(_COM_RECEIVE,1,0);
    fwrite(&r,1,1,fpw);


  }

  while (*ptr4 != NULL) {
 _bios_serialcom(_COM_SEND,1,*ptr4);
  ptr4++;
  }


  r=' ';
 while(r  != '*') {
    com_status= _bios_serialcom(_COM_STATUS,1,0);
    printf("COM2 Status:0x% .4x \n", com_status);

       r=_bios_serialcom(_COM_RECEIVE,1,0);
    fwrite(&r,1,1,fpw);


  }
     fcloseall();
}
```

```
**************************************************************
```

'C' program to run test experiment
Program name: TEST

```
**************************************************************
```

```
#include <bios.h>
#include <stdio.h>
#define  DATA_READY 0x0100;

unsigned int _bios_serialcom(unsigned int, unsigned int, unsigned int);
void main()
{

FILE *fpw;      /*pointer for the write file*/

char command1[]="DCL;SIE 15;CELL 1;MODE 1;S/P 300; TMB
50000\n";
char *ptr1 ;
char command2[]="PAM 1;IRMODE 3;SETI -350 -3;TP;DO
25;TP;RUERR;LOOP\n";
char *ptr2 ;
char command3[]="CELL 0\n";
char *ptr3 ;

unsigned int r;
unsigned int com_status;
int i;
   fpw=fopen("TEST.dat","w");
   ptr1=command1;
   ptr2=command2;
   ptr3=command3;


   com_status=_bios_serialcom(_COM_STATUS,1,0);
   printf("COM2 Status:0x% .4x \n", com_status);
   _bios_serialcom(_COM_INIT,1,_COM_CHR8 |
                           _COM_STOP1 | _COM_NOPARITY |
                           _COM_300);
```

```
 while (*ptr1 != NULL) {
_bios_serialcom(_COM_SEND,1,*ptr1);
 ptr1++;
}


i=0;
r=' ';
while(r  != '*') {
   com_status= _bios_serialcom(_COM_STATUS,1,0);
   printf("COM2 Status:0x% .4x \n", com_status);

      r=_bios_serialcom(_COM_RECEIVE,1,0);
  fwrite(&r,1,1,fpw);


}
while (*ptr2 != NULL) {
_bios_serialcom(_COM_SEND,1,*ptr2);
 ptr2++;
}


 r=' ';
while(r  != '*') {
   com_status= _bios_serialcom(_COM_STATUS,1,0);
   printf("COM2 Status:0x% .4x \n", com_status);

      r=_bios_serialcom(_COM_RECEIVE,1,0);
  fwrite(&r,1,1,fpw);


}
while (*ptr3 != NULL) {
_bios_serialcom(_COM_SEND,1,*ptr3);
 ptr3++;
}
```

```
  r=' ';
  while(r  != '*') {
     com_status= _bios_serialcom(_COM_STATUS,1,0);
     printf("COM2 Status:0x% .4x \n", com_status);

        r=_bios_serialcom(_COM_RECEIVE,1,0);
     fwrite(&r,1,1,fpw);


  }
      fcloseall();
}
```

```
**********************************************************

          'C' program to run polarization experiment
                    Program name: POLA
**********************************************************


#include <bios.h>
#include <stdio.h>
#define  DATA_READY 0x0100;

unsigned int _bios_serialcom(unsigned int, unsigned int, unsigned int);
void main()
{

FILE *fpw;      /*pointer for the write file*/

char command1[]="DCL;SIE 15;CELL 1;MODE 1;S/P 600; TMB
50000\n";
char *ptr1 ;
char command2[]="PAM 1;IRMODE 3;SETI -0 -3;TP;DO
5;TP;RUERR;LOOP\n";
char *ptr2 ;
char command3[]="SETI -5 -3;TP;DO 10;TP;RUERR;LOOP\n";
char *ptr3 ;
char command4[]="SETI -10 -3;TP;DO 10;TP;RUERR;LOOP\n";
char *ptr4 ;
char command5[]="SETI -25 -3;TP;DO 10;TP;RUERR;LOOP\n";
char *ptr5 ;
char command6[]="SETI -50 -3;TP;DO 10;TP;RUERR;LOOP\n";
char *ptr6 ;
char command7[]="SETI -100 -3;TP;DO 15;TP;RUERR;LOOP\n";
char *ptr7 ;
char command8[]="SETI -250 -3;TP;DO 15;TP;RUERR;LOOP\n";
char *ptr8 ;
char command9[]="SETI -350 -3;TP;DO 15;TP;RUERR;LOOP\n";
char *ptr9 ;
char command10[]="SETI -500 -3;TP;DO 15;TP;RUERR;LOOP\n";
char *ptr10 ;
char command11[]="SETI -600 -3;TP;DO 15;TP;RUERR;LOOP\n";
char *ptr11 ;
char command12[]="SETI -750 -3;TP;DO 15;TP;RUERR;LOOP\n";
```

```
char *ptr12 ;
char command13[]="SETI -900 -3;TP;DO 15;TP;RUERR;LOOP\n";
char *ptr13 ;
char command14[]="SETI -1000 -3;TP;DO 15;TP;RUERR;LOOP;CELL
0\n";
char *ptr14 ;
unsigned int r;
unsigned int com_status;
int i;
   fpw=fopen("pola.dat","w");
   ptr1=command1;
   ptr2=command2;
   ptr3=command3;
   ptr4=command4;
   ptr5=command5;
   ptr6=command6;
   ptr7=command7;
   ptr8=command8;
   ptr9=command9;
   ptr10=command10;
   ptr11=command11;
   ptr12=command12;
   ptr13=command13;
   ptr14=command14;

   com_status=_bios_serialcom(_COM_STATUS,1,0);
   printf("COM2 Status:0x% .4x \n", com_status);
   _bios_serialcom(_COM_INIT,1,_COM_CHR8 |
                              _COM_STOP1 | _COM_NOPARITY |
                              _COM_300);


   while (*ptr1 != NULL) {
  _bios_serialcom(_COM_SEND,1,*ptr1);
   ptr1++;
   }


  i=0;
  r=' ';
  while(r  != '*') {
     com_status= _bios_serialcom(_COM_STATUS,1,0);
```

```
   printf("COM2 Status:0x% .4x \n", com_status);

      r=_bios_serialcom(_COM_RECEIVE,1,0);
  fwrite(&r,1,1,fpw);


}
while (*ptr2 != NULL) {
_bios_serialcom(_COM_SEND,1,*ptr2);
 ptr2++;
}


 r=' ';
while(r  != '*') {
   com_status= _bios_serialcom(_COM_STATUS,1,0);
   printf("COM2 Status:0x% .4x \n", com_status);

      r=_bios_serialcom(_COM_RECEIVE,1,0);
  fwrite(&r,1,1,fpw);


}
while (*ptr3 != NULL) {
_bios_serialcom(_COM_SEND,1,*ptr3);
 ptr3++;
}


 r=' ';
while(r  != '*') {
   com_status= _bios_serialcom(_COM_STATUS,1,0);
   printf("COM2 Status:0x% .4x \n", com_status);

      r=_bios_serialcom(_COM_RECEIVE,1,0);
  fwrite(&r,1,1,fpw);


}

 while (*ptr4 != NULL) {
_bios_serialcom(_COM_SEND,1,*ptr4);
```

```
 ptr4++;
}


 r=' ';
while(r  != '*') {
   com_status= _bios_serialcom(_COM_STATUS,1,0);
   printf("COM2 Status:0x% .4x \n", com_status);

      r=_bios_serialcom(_COM_RECEIVE,1,0);
  fwrite(&r,1,1,fpw);


}

while (*ptr5 != NULL) {
_bios_serialcom(_COM_SEND,1,*ptr5);
 ptr5++;
}


 r=' ';
while(r  != '*') {
   com_status= _bios_serialcom(_COM_STATUS,1,0);
   printf("COM2 Status:0x% .4x \n", com_status);

      r=_bios_serialcom(_COM_RECEIVE,1,0);
  fwrite(&r,1,1,fpw);


}
while (*ptr6 != NULL) {
_bios_serialcom(_COM_SEND,1,*ptr6);
 ptr6++;
}


 r=' ';
while(r  != '*') {
   com_status= _bios_serialcom(_COM_STATUS,1,0);
   printf("COM2 Status:0x% .4x \n", com_status);
```

```
      r=_bios_serialcom(_COM_RECEIVE,1,0);
   fwrite(&r,1,1,fpw);


}
while (*ptr7 != NULL) {
_bios_serialcom(_COM_SEND,1,*ptr7);
 ptr7++;
}


 r=' ';
while(r  != '*') {
    com_status= _bios_serialcom(_COM_STATUS,1,0);
    printf("COM2 Status:0x% .4x \n", com_status);

      r=_bios_serialcom(_COM_RECEIVE,1,0);
   fwrite(&r,1,1,fpw);


}
while (*ptr8 != NULL) {
_bios_serialcom(_COM_SEND,1,*ptr8);
 ptr8++;
}


 r=' ';
while(r  != '*') {
    com_status= _bios_serialcom(_COM_STATUS,1,0);
    printf("COM2 Status:0x% .4x \n", com_status);

      r=_bios_serialcom(_COM_RECEIVE,1,0);
   fwrite(&r,1,1,fpw);


}
while (*ptr9 != NULL) {
_bios_serialcom(_COM_SEND,1,*ptr9);
 ptr9++;
}
```

```
r=' ';
while(r  != '*') {
   com_status= _bios_serialcom(_COM_STATUS,1,0);
   printf("COM2 Status:0x% .4x \n", com_status);

      r=_bios_serialcom(_COM_RECEIVE,1,0);
  fwrite(&r,1,1,fpw);


}
while (*ptr10 != NULL) {
_bios_serialcom(_COM_SEND,1,*ptr10);
 ptr10++;
}


r=' ';
while(r  != '*') {
   com_status= _bios_serialcom(_COM_STATUS,1,0);
   printf("COM2 Status:0x% .4x \n", com_status);

      r=_bios_serialcom(_COM_RECEIVE,1,0);
  fwrite(&r,1,1,fpw);


}
while (*ptr11 != NULL) {
_bios_serialcom(_COM_SEND,1,*ptr11);
 ptr11++;
}


r=' ';
while(r  != '*') {
   com_status= _bios_serialcom(_COM_STATUS,1,0);
   printf("COM2 Status:0x% .4x \n", com_status);

      r=_bios_serialcom(_COM_RECEIVE,1,0);
  fwrite(&r,1,1,fpw);
```

```
}
while (*ptr12 != NULL) {
_bios_serialcom(_COM_SEND,1,*ptr12);
 ptr12++;
}


 r=' ';
while(r  != '*') {
   com_status= _bios_serialcom(_COM_STATUS,1,0);
   printf("COM2 Status:0x% .4x \n", com_status);

      r=_bios_serialcom(_COM_RECEIVE,1,0);
  fwrite(&r,1,1,fpw);


}
while (*ptr13 != NULL) {
_bios_serialcom(_COM_SEND,1,*ptr13);
 ptr13++;
}


 r=' ';
while(r  != '*') {
   com_status= _bios_serialcom(_COM_STATUS,1,0);
   printf("COM2 Status:0x% .4x \n", com_status);

      r=_bios_serialcom(_COM_RECEIVE,1,0);
  fwrite(&r,1,1,fpw);


}
while (*ptr14 != NULL) {
_bios_serialcom(_COM_SEND,1,*ptr14);
 ptr14++;
}


 r=' ';
while(r  != '*') {
   com_status= _bios_serialcom(_COM_STATUS,1,0);
```

```
    printf("COM2 Status:0x% .4x \n", com_status);

       r=_bios_serialcom(_COM_RECEIVE,1,0);
    fwrite(&r,1,1,fpw);


  }
     fcloseall();
}
```

APPENDIX - B

(Polarization data for various electrodes)

Current, mA	Potential, mV	IR comp	IR free pot.	C. D. mA/cm2	Over pot. mV
0	-907	0	-907	0	0
-5	-902	5	-907	0.83	0
-11	-898	7	-905	1.83	2
-26	-885	17	-902	4.33	5
-50	-865	30	-895	8.33	12
-101	-823	60	-883	16.83	24
-251	-705	145	-850	41.83	57
-351	-626	195	-821	58.5	86
-500	-506	278	-784	83.33	123
-600	-425	336	-761	100	146
-750	-305	421	-726	125	181
-900	-185	512	-697	150	210
-1000	-50	624	-674	166.67	233

Polarization Data for conventionally stabilized catalysts

Current,mA	Potential,mV	IR comp	IR free pot.	C.D. mA/cm2	Over Poten, mV
0	-900	0	-900	0	0
-5	-896	4	-900	0.83	0
-11	-892	7	-899	1.83	1
-26	-879	16	-895	4.33	5
-50	-857	27	-884	8.33	16
-100	-812	54	-866	16.67	34
-250	-675	136	-811	41.67	89
-351	-584	186	-770	58.5	130
-500	-457	270	-727	83.33	173
-600	-375	326	-701	100	199
-750	-254	412	-666	125	234
-900	-130	503	-633	150	267
-1000	-30	574	-604	166.67	296

Polarization Data for 5 wt.% H_2O_2 stabilized catalyst

current, mA	potential, mV	IR comp	IR free pot	C. D. mA/cm2	Over Pot, mV
0	-904	0	-904	0	0
-6	-900	2	-902	1	2
-11	-896	7	-903	1.83	1
-26	-883	15	-898	4.33	6
-51	-861	30	-891	8.5	13
-100	-815	56	-871	16.67	33
-251	-673	143	-816	41.83	88
-351	-603	195	-798	58.5	106
-500	-483	281	-764	83.33	140
-601	-395	337	-732	100.17	172
-601	-378	337	-715	100.17	189
-750	-277	425	-702	125	202
-900	-146	509	-655	150	249
-1000	-74	566	-640	166.67	264

Polarization Data for 10 wt.% H_2O_2 stabilized catalyst

Current, mA	Potential, mV	IR comp	IR free pot	C.D. mA/cm2	Over Pot, mV
0	-903	0	-903	0	0
-5	-900	3	-903	0.83	0
-11	-896	7	-903	1.83	0
-26	-885	17	-902	4.33	1
-50	-865	32	-897	8.33	6
-100	-825	61	-886	16.67	17
-251	-704	145	-849	41.83	54
-350	-623	204	-827	58.33	76
-500	-501	292	-793	83.33	110
-601	-424	348	-772	100.17	131
-750	-310	437	-747	125	156
-900	-199	528	-727	150	176
-1000	-124	587	-711	166.67	192

Polarization Data for 15 wt.% H_2O_2 stabilized catalyst

Current, mA	Potential, mV	IR comp	IR free pot.	C.D.mA/cm2	Over Pot. mV
0	-900	0	-900	0	0
-5	-897	3	-900	0.83	0
-11	-891	8	-899	1.83	1
-26	-882	15	-897	4.33	3
-50	-862	30	-892	8.33	8
-100	-826	54	-880	16.67	20
-251	-698	140	-838	41.83	62
-350	-632	186	-818	58.33	82
-500	-499	267	-766	83.33	119
-600	-400	360	-760	100	140
-750	-296	437	-733	125	167
-900	-198	506	-704	150	196
-1000	-95	570	-683	166.67	217

Polarization Data for 25 wt.% H_2O_2 stabilized catalyst

Current, mA	Potential, mV	IR comp	IR free poten.	C. D. mA/cm2	Over pot. mV
0	-900	0	-900	0	0
-6	-895	3	-898	1	2
-11	-890	7	-897	1.83	3
-26	-875	18	-893	4.33	7
-51	-849	30	-879	8.5	21
-101	-794	57	-851	16.83	49
-251	-641	137	-778	41.83	122
-351	-558	189	-747	58.5	153
-500	-441	270	-711	83.33	189
-601	-363	320	-683	100.17	217
-750	-247	405	-652	125	248
-900	-126	502	-628	150	272
-1000	-49	560	-609	166.67	291

Polarization Data for low flow rate Oxygen stabilized catalyst

Current, mA	Potential, mV	IR comp	IR free poten.	C. D. mA/cm2	Over pot. mV
0	-901	0	-901	0	0
-6	-897	3	-900	1	1
-11	-892	8	-900	1.83	1
-26	-878	16	-894	4.33	7
-51	-853	29	-882	8.5	19
-101	-804	57	-861	16.83	40
-251	-653	141	-794	41.83	107
-351	-563	194	-757	58.5	144
-500	-448	270	-718	83.33	183
-601	-367	324	-691	100.17	210
-750	-243	412	-655	125	246
-900	-136	500	-636	150	265
-1001	-30	581	-611	166.83	290

Polarization Data for high flow rate Oxygen stabilized catalyst

Current, mA	Potential, mV	IR comp	IR free pot.	C. D. mA/cm2	Over pot, mV
0	-906	0	-906	0	0
-6	-903	3	-906	1	0
-11	-898	8	-906	1.83	0
-26	-883	16	-899	4.33	7
-51	-857	29	-886	8.5	20
-101	-801	55	-856	16.83	50
-251	-649	130	-779	41.83	127
-351	-564	183	-747	58.5	159
-500	-446	259	-705	83.33	201
-601	-364	320	-684	100.17	222
-750	-244	412	-656	125	250
-900	-130	500	-630	150	276
-1000	-43	565	-608	166.67	298

Polarization Data for Air stabilized catalyst